

Addition and Cyclization Reactions in the Thermal Conversion of Hydrocarbons with an Enyne Structure, 7^[†]

Cycloisomerization of 1-Phenyl-1-buten-3-yne to Naphthalene via Cinnamylidene Carbenes – A Complex Reaction Involving 1,2-C Switches and 1,2-Styryl Migrations

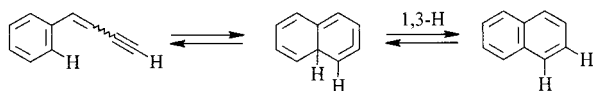
Kathrin Schulz,^[a] Jörg Hofmann,^[a,b] and Gerhard Zimmermann*^[a,b]

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The thermal conversion of [4-¹³C,4-D]- (**1**) and [4-¹³C]-1-phenyl-1-buten-3-yne (**7**) has been studied in a quartz tubular reactor at 650 °C (**1**, in the presence of N₂ and N₂/toluene, respectively) and at 600 and 620 °C (mixture of **1** and **7**, in N₂ only) at a reaction time of approximately 0.3 s. The liquid pyrolyzates were analyzed spectroscopically. By means of a special calculation method reported recently, the naphthalene isotopomers formed by reaction pathways other

than those proceeding via cinnamylidene carbenes were arithmetically eliminated and the reaction events proceeding via carbene intermediates were mechanistically analyzed. The result of this analysis undoubtedly suggests a complex reaction in which the rates of the partial reactions may be placed in the following order: 1,2-D(H) >> 1,2-styryl > 1,6-C,H.

1,3-Hexadien-5-yne, in which one or both of the C–C double bonds of the dienyli skeleton are integral parts of 6π-systems, have turned out to be useful precursors in high-temperature syntheses of planar^[2] and bowl-shaped^[3] polycyclic aromatics. At first glance, cycloisomerizations of this type seem to follow a simple mechanistic pattern, as depicted in Scheme 1. However, sophisticated experiments aimed at proving other pathways, which are envisaged as occurring competitively in the thermal conversion of 1-phenyl-1-buten-3-yne, clearly show that this is indeed the case at temperatures between 550 and 750 °C.^[1,2c,4,5] There is no longer any doubt that electrocyclic ring closures^[6] and cyclization steps proceeding via alkylidenecarbenes (cf. for example, refs.^{[2][3]}) as well as via vinyl-type radicals^[1,2c,4] compete not only with each other, but also with carbene-mediated 1,2-C switches within the enyne fragment of the employed phenylbutenyne,^[5] which are themselves independently operative in the preliminary stages of the naphthalene formation.



Scheme 1. Naphthalene formation by electrocyclic ring closure

[†] Part 6: Ref.^[1]

[a] Abteilung Hochtemperaturreaktionen am Institut für Technische Chemie der Universität Leipzig, Permoserstraße 15, D-04303 Leipzig, Germany
Fax: (internat.) +49(0)341/235–2701
E-mail: zimmerma@sonne.tachemie.uni-leipzig.de

[b] Present address: Institut für Nichtklassische Chemie an der Universität Leipzig, Permoserstraße 15, D-04303 Leipzig, Germany

Although the mechanistic details of the formation of 6π-ring systems by electrocyclic ring closure and the subsequent 1,5(1,3)-H shift^[6] are now known, this route is in fact almost negligible if the terminal C–C double bond of the 1,3-hexadien-5-yne is part of a phenyl group. This is because in the cyclization step the resonance stabilization energy of the phenyl group has to be overcome.^[4] Subsequently, the thermal conversion in question is mainly supported by the vinyl radical and, at higher temperatures, by reversibly formed carbenes. Both routes represent intrinsically complex reactions. Their details, however, are as yet only well-known for the radical cycloisomerizations.^[1] A coherent analysis of the complex reaction controlled by the corresponding cinnamylidene carbenes is not yet available, though some important features are already known.^[2c,3c,4,5]

Against this background, we became interested in delineating a more complete picture by carrying out further studies in this field. We report herein on repeatedly performed thermal conversions of [4-¹³C,4-D]-1-phenyl-1-buten-3-yne **1** (cf. ref.^[1]) at 650 °C in the presence of nitrogen and nitrogen/toluene, respectively, as well as on the co-pyrolysis of a mixture of **1** and [4-¹³C]-1-phenyl-1-buten-3-yne **7** at 600 and 620 °C, in this case exclusively in the presence of nitrogen. The results are discussed in relation to already published mechanistic assumptions and proposals.

Results

Thermal Conversion of [1-¹³C,4-D]-1-Phenyl-1-buten-3-yne (**1**)

Labelled 1-phenyl-1-buten-3-yne (**1**) was available from our earlier research^[1] and was used as a 1:99 *cis/trans* mix-

ture (GC purity: 98.6%, D and ^{13}C content: 99 atom-% each). It was used directly as the starting compound for the pyrolysis experiments in the form of a 10% solution in benzene.

In each run, between 0.7 and 0.9 mL of this solution was slowly evaporated into a stream of nitrogen (N_2) gas or a nitrogen/toluene vapour mixture (N_2/tol), respectively. Principally, the gas streams served as diluents (d) carrying **1** in low concentrations ($n_d/n_1 \approx 50:1$) through a quartz flow system (cf. for example, ref.^[2c]). The reaction temperature was 650°C, and the reaction time was calculated to be approximately 0.3 s. Under the applied conditions, however, the nitrogen/toluene mixture served not only as a diluent but also as an auxiliary agent lowering the stationary concentrations of the unavoidably formed chain carrier radicals.^[4] The effluents were cooled, collected, and analyzed by GC/FID, GC/FT-IR, GC/MS, ^1H , ^2H , and ^{13}C NMR as detailed previously.^{[1][5]} The yields of the liquid pyrolyzates (essentially isotopomers of naphthalene, benzofulvene, azulene, and phenylbutenyne) boiling at temperatures higher than benzene amounted to $\geq 95\%$ of the solution employed in each case. With strictly comparable parameters, each of the experiments was repeated to guarantee the reproducibility of the composition of the formed isotopomers in the liquid pyrolyzates. The results, representing averaged values for each compound, are listed in Table 1. The product compositions of the fractions (upper part) were analyzed by GC and GC/MS. The proportions of the remaining **1** and its isotopomers (**2**, **7**, **8**) were calculated from the corresponding ^1H - and ^{13}C -NMR as well as GC/FT-IR spectra of the liquid pyrolyzates according to ref.^[5], while the proportions of the naphthalene isotopomers **5**, **6**, **11**, and **12** as well as those of $[1-^{13}\text{C},1\text{-D}]$ - and $[2-^{13}\text{C},1\text{-D}]$ naphthalene were determined solely from the ^{13}C -NMR data (see, for example, ref.^[1] and the Experimental Section). The percentage of each component in the liquid pyrolyzates of the repeated experiments varied only marginally. The deviations were estimated to be $\pm 2\%$ absolute at most, referred to the average values listed in Table 1.

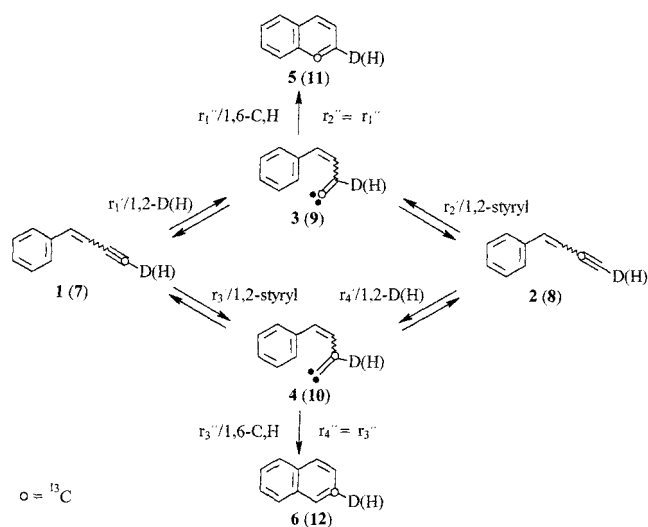
Thermal Conversion of a Mixture of $[1-^{13}\text{C},4\text{-D}]\text{-1-Phenyl-1-buten-3-yne}$ (**1**) and $[1-^{13}\text{C}]\text{-1-Phenyl-1-buten-3-yne}$ (**7**)

To check the role that primary kinetic H/D isotope effects may play in the reaction cascade according to Scheme 2, a 10% benzene solution of a 46:54 mixture of **1** and **7** was thermally converted in nitrogen. Experiments were carried out at 600 and 620°C (0.3 s) only to guarantee that the found composition of the phenylbutenyne isotopomer fraction is still far below the equilibration point, which is known to be reached at approximately 750°C.^[5] The experiments were carried out in the same way as described previously for the thermal conversion of **1**, with the same parameter ranges. The obtained results are compiled in Tables 2.1 and 2.2.

Table 1. Dependence of the products formed from **1** in the presence of N_2 and N_2/tol at 650°C

diluent		N ₂	N ₂ -tol ^[a]
product fraction ^[b]			
1-phenyl-1-buten-3-yne		82	90
naphthalenes		15	8.5
1-methylene-1 <i>H</i> -indenes		≈ 2	-
azulenes		≤ 1	≈ 1
proportions of the isotopomers in the 1-phenyl-1-buten-3-yne fraction (= 100 %)			
[4- ¹³ C,4-D]-	1	66	65.5
[3- ¹³ C,4-D]-	2	33	33
[4- ¹³ C]-	7	≤ 1 ^[c]	< 1
[3- ¹³ C]-	8		
proportions of the isotopomers in the naphthalene fraction (= 100 %)			
[1- ¹³ C,2-D]-	5	33	51
[2- ¹³ C,2-D]-	6	32	27
[1- ¹³ C]-	11	8	5
[2- ¹³ C]-	12	8	4
[1- ¹³ C,1-D]-		14	10
[2- ¹³ C,1-D]-		5	3

^[a] 5 mol-% toluene in nitrogen. – ^[b] In % of the liquid pyrolyzate [minus benzene (solvent)]. – ^[c] At 750°C in the presence of hydrogen, the proportion of **7** + **8** amounts only to $\leq 3\%$.



Scheme 2. Main reaction cascades in the conversion of **1** (**7**)

Table 2.1. Degrees of conversion and selectivities of the formed products ($S^{[a]}$) in the thermal conversion of a mixture of **1** and **7**^[b] at 600 and 620 °C in the presence of nitrogen

Temperature [°C]	600	620
Degree of conversion (%) ^[c]	6	9
Product selectivities (S):		
Naphthalenes	96	91
1-Methylene-1 <i>H</i> -indenes	3	8
Azulenens	1	1
Others	trace	trace

^[a] S = mol of product formed from 100 mol of the fed sum of **1** + **7** converted. – ^[b] Percentage composition of the 1-phenyl-1-buten-3-yne **1/7** = 46:54. – ^[c] Referred to the sum of **1** + **7** introduced.

Table 2.2. Composition of the remaining phenylbutenyne and the formed naphthalene fraction (= 100% each) in the pyrolyzates of the copolyolysis of **1** + **7** according to the summarized data given in Table 2.1

Temperature [°C]		600	620
1-Phenyl-1-buten-3-yne ^[a] :			
[4- ¹³ C,4-D]-	(1)	39	34.5
[3- ¹³ C,4-D]-	(2)	7.5	11
[4- ¹³ C]-	(7)	45	41
[3- ¹³ C]-	(8)	8.5	13.5
Naphthalenes ^[a] :			
[1- ¹³ C,2-D]-	(5)	ca. 17	ca. 16
[2- ¹³ C,2-D]-	(6)	ca. 12	ca. 13
[1- ¹³ C]-	(11)	ca. 39	ca. 37
[2- ¹³ C]-	(12)	ca. 25	ca. 26.5
[1- ¹³ C,1-D]-		ca. 6	ca. 6
[2- ¹³ C,1-D]-		< 1	ca. 1.5

^[a] The composition was calculated on the basis of characteristic spectroscopic data of the corresponding pyrolyzate components (cf. Experimental Section and ref.^[11])

Calculation of the Amounts of the Naphthalenes **5** and **6** Formed via Cinnamylidenecarbenes

Of the six naphthalene isotopomers listed in Table 1, only two of them can in fact be straightforwardly formed via cinnamylidenecarbenes, i.e. **5** and **6** (cf. Scheme 2), but, unfortunately, the matter is more complicated as they can also be formed by radical-controlled ring closures.^[1]

Therefore, the percentages of **5** and **6** immediately formed from the cinnamylidene carbenes **3** and **4**, respectively, have to be calculated as the difference between the molar percentages of **5** (**[5]**) and **6** (**[6]**), respectively, in the corresponding liquid pyrolyzate, and the amounts formed through vinyl-type radicals.^[1]

For this, we used the computational method detailed in ref.^[4], starting from the experimental results obtained in the thermal conversion of 1-phenyl-1-buten-3-yne in the presence of diluent gases of different nature, and using Equation 1 with $x = 5$ and **6**, respectively. The results obtained in this way are compiled in Table 3.

Table 3. Molar percentages $[x]$ with $x = 5$ and **6** available in the pyrolyzates from **1** and formed by radical ($[x]_{\text{rad}}$) and carbene-like processes ($[x]_{\text{carb}}$) in the presence of both N_2 and N_2/tol at 650 °C

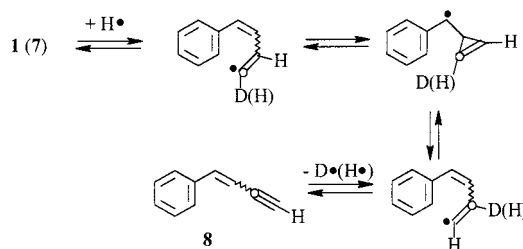
naphthalenes x	$[x]_{N_2}$	$[x]_{N_2/\text{tol}}$	$[x]_{\text{rad},N_2}$	$[x]_{\text{rad},N_2/\text{tol}}$	$[x]_{\text{carb}}$
5	4.7	3.9	1.1	0.3	3.6
6	4.8	2.25	3.5	0.95	1.3

$$[x]_{\text{carb}} = [x] - [x]_{\text{rad}} \quad (1)$$

Discussion

The product balance of the liquid pyrolyzates from the conversion of **1** at 650 °C (Table 1) clearly reveals that the sum of the formed compounds having a structure fundamentally different from that of **1** amounts to just 18 and 10%, with naphthalene as the main product. Of the remainder, the 1-phenyl-1-buten-3-yne fraction consists of a mixture of four (**1**, **2**, **7**, and **8**) and the naphthalene fraction a mixture of six isotopomers (**5**, **6**, **11**, **12**, [1-¹³C,1-D]- and [2-¹³C,1-D]naphthalene).

Taking the composition of the 1-phenyl-1-buten-3-yne fraction into account, it immediately becomes clear that the observed automerization $\mathbf{1} \rightleftharpoons \mathbf{2}$ cannot be a radical-assisted process like that for which the mechanism is outlined in Scheme 3. If such a process were to be operative, a significant dedeuteration of **1** and **2** ought to be expected. The non-deuterated ¹³C-phenylbutenyne **7** and **8** are, however, formed only in trace amounts. This supports our previously drawn conclusion, according to which the automerization $\mathbf{1} \rightleftharpoons \mathbf{2}$ runs as a cyclic quadrangular process as outlined in the core of Scheme 2. The formation of **2** from **1** constitutes the main reaction event at 650 °C. Consequently, the 1,2-D and even the 1,2-styryl migration are undoubtedly much more favored compared to the 1,6-C,H insertion of the carbenes **3**, **4** and **9**, **10** into the naphthalenes **5**, **6** and **11**, **12**, respectively.



Scheme 3. Considered radical mechanism of the automerization $\mathbf{1} \rightleftharpoons \mathbf{2}$

This observation is somewhat surprising because it seems to be tacitly accepted that the activation parameters of the unimolecularly occurring 1,5- and 1,6-C,H insertion (but not the 1,4-C,H insertion^[7]) of the corresponding alkenylidene carbenes are considered to be almost negligible in comparison to those for the 1,2-R migration.^{[7][8]} This assumption is, however, speculative since experiment-based activation parameters of unimolecularly proceeding 1,5- and

Table 4. Molar proportions of **5** and **6** formed in the pyrolysis of **1** from **1** and **2** by 1,2-D and 1,2-styryl migrations in the presence of nitrogen and nitrogen/toluene, respectively, at 650 °C (0.3 s)

Product	Parent compound	Formed according to	mol-% formed via carbene species	Calculated by Equation
5	1	$r_1'(1,2\text{-D}) + r_1''(1,6\text{-C,H})$	3.57	4
6	2	$r_4'(1,2\text{-D}) + r_4''(1,6\text{-C,H})$	1.08	9
6	2	$r_3'(1,2\text{-styryl}) + r_3''(1,6\text{-C,H})$	0.20	5
5	1	$r_2'(1,2\text{-styryl}) + r_2''(1,6\text{-C,H})$	0.06	8

1,6-C,H insertions of alkenylidenecarbenes have still to be reported. The preceding reflections clearly show that the mechanism of the naphthalene formation from 1-phenyl-1-buten-3-yne can only be adequately discussed when it is known how the preceding automerization process works. Therefore, the proportions of **5** and **6** formed from the carbene intermediates **3** and **4** should be considered first.

In accordance with the data listed in Table 3, approximately 4.9 mol-% of the combined total amount of **5** and **6** is generated from **3** and **4**. This corresponds to about 30% in the presence of nitrogen and 60% in the presence of nitrogen/toluene. In this process (cf. Scheme 2), **5** is formed from **1** by the partial reaction $r_1' + r_1'' (= r_1)$ and from **2** by $r_2' + r_2'' (= r_2)$. Therefore,

$$[\mathbf{5}]_{\text{carb}} = [\mathbf{r}_1 \mathbf{5}] + [\mathbf{r}_2 \mathbf{5}] \quad (2)$$

and, by analogy,

$$[\mathbf{6}]_{\text{carb}} = [\mathbf{r}_3 \mathbf{6}] + [\mathbf{r}_4 \mathbf{6}] \quad (3)$$

holds for the formation of **6**, where the index r_i in $[\mathbf{r}_i \mathbf{x}]$ denotes the reaction steps from **1** and **2** to $\mathbf{x} = \mathbf{5}$ and $\mathbf{x} = \mathbf{6}$, respectively.

Taking into account that the average percentages in which **1** and **2** are available in the reactor volume depend on the residence time effective at every differential reactor segment,^[1] and assuming that $^{12}\text{C}/^{13}\text{C}$ isotope effects are consistently very small, the molar portions $[\mathbf{r}_1 \mathbf{5}]$ and $[\mathbf{r}_2 \mathbf{5}]$ have to be larger than those of $[\mathbf{r}_3 \mathbf{6}]$ and $[\mathbf{r}_4 \mathbf{6}]$ by the factor $R_{\text{eff}}^{[9]}$ defined as the ratio of the steady-state concentrations at which **1** and **2** become effective in the whole reactor.^[1]

Therefore, it holds that

$$[\mathbf{r}_1 \mathbf{5}] = R_{\text{eff}} \cdot [\mathbf{r}_4 \mathbf{6}] \quad (4)$$

and

$$[\mathbf{r}_3 \mathbf{6}] = R_{\text{eff}} \cdot [\mathbf{r}_2 \mathbf{5}] \quad (5)$$

which finally gives the following system of Equations:

$$[\mathbf{5}]_{\text{carb}} = R_{\text{eff}} \cdot [\mathbf{r}_4 \mathbf{6}] + [\mathbf{r}_2 \mathbf{5}] \quad (6)$$

$$[\mathbf{6}]_{\text{carb}} = [\mathbf{r}_4 \mathbf{6}] + R_{\text{eff}} \cdot [\mathbf{r}_2 \mathbf{5}] \quad (7)$$

the solutions of which are described by Equations 8 and 9.^[10]

$$[\mathbf{r}_2 \mathbf{5}] = \frac{[\mathbf{5}]_{\text{carb}} - R_{\text{eff}} \cdot [\mathbf{6}]_{\text{carb}}}{1 - R_{\text{eff}}^2} \quad (8)$$

$$[\mathbf{r}_4 \mathbf{6}] = \frac{[\mathbf{6}]_{\text{carb}} - R_{\text{eff}} \cdot [\mathbf{5}]_{\text{carb}}}{1 - R_{\text{eff}}^2} \quad (9)$$

The molar proportions of **5** and **6** formed from **1** according to the reaction steps $r_1' + r_1'' (= r_1)$ and from **2** according to $r_2' + r_2'' (= r_2)$ were calculated from the experimentally determined proportions of **5** and **6** in the liquid pyrolyzates. The results obtained in this way are summarized in Table 4.

From the above data, it can be concluded unequivocally that the formation of **5** and **6** from **1** and **2** is predetermined to approximately 95% by 1,2-D ($r_1 + r_4$) and to only about 5% by 1,2-styryl migrations ($r_2 + r_3$).

This statement seems to be largely in line with Dreiding's observation,^[11] according to which the thermal cyclization of [3- ^{13}C]-1-(1-methylcyclopentyl)-2-propynone at 530 °C occurs almost exclusively by 1,2-H shift and 1,5-C,H insertion reactions of the initially formed carbene species, while the alternative 1,2-acyl migration becomes important only at higher temperatures.

To round off this picture, it is worthwhile to gain some insight into the relative rates at which the reversed 1,2-D and the 1,2-styryl migration as well as the 1,6-C,H insertion compete with each other when starting from the corresponding carbene intermediates **3** and **4**. To this end, the results of the copyrolysis of **1** and **7** (Tables 2.1 and 2.2) were analyzed.

Taking the different portions of **1** and **7** in the feedstock mixture into account, the data in Table 2.2 clearly reveal that the automerizations $\mathbf{1} \rightleftharpoons \mathbf{2}$ and $\mathbf{7} \rightleftharpoons \mathbf{8}$ proceed at almost the same rate under intrinsic conditions. A kinetic H/D isotope effect is not measurable. The formed cinnamylidenecarbenes **3**, **4** and **9**, **10** (from **7**, **8**) evidently undergo a back reaction at a rate much faster than the 1,2-styryl migrations. Consequently, the 1,2-styryl and not the 1,2-D(H) migrations must be the rate-determining step of the 1,2-C switches.

From the same experiment, the molar proportion of **2** has been determined to be significantly higher (31%) than the sum of the molar proportions of the naphthalenes **5** and **6** in the liquid pyrolyzate formed from **1** via cinnamylidene carbenes at 650 °C, which amounts only to just less than 5% (Table 3, column 6). Despite the lack of kinetic data for the

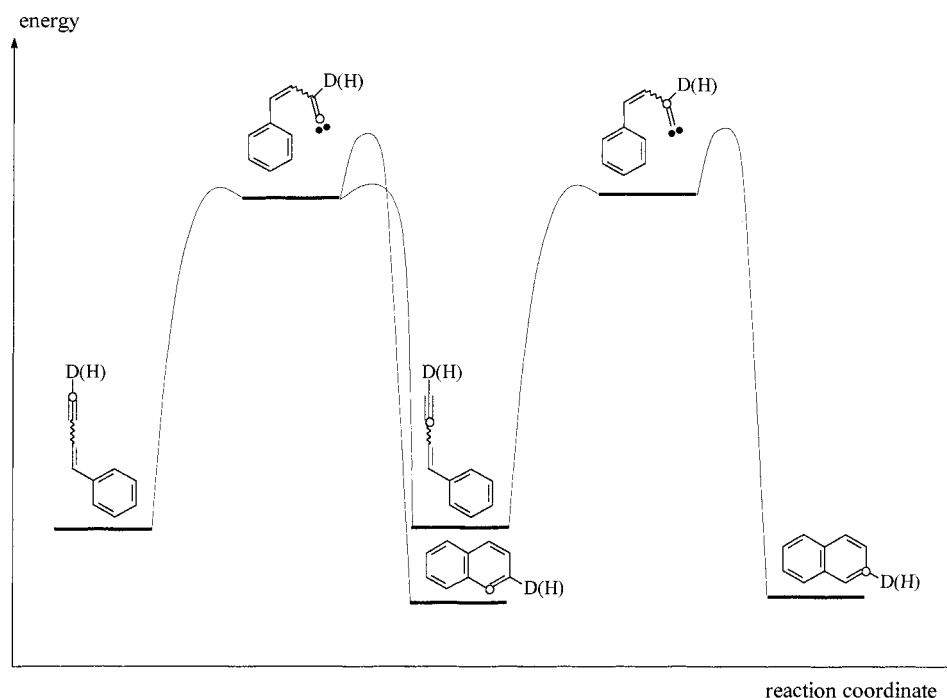
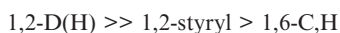


Figure 1. Energy profile diagram

1,2-styryl migrations and 1,6-C,H insertions, the proportions of **5** and **2** in the liquid pyrolyzate from **1** make it possible to roughly assess the ratio of the rate constants at which **5** and **2** are formed from the common precursor **3**, provided that the consecutive reaction of **2** to **4** and its subsequent reactions are ignored. Under this assumption, the 1,2-styryl migration of **3** to **2** is estimated to be faster than the 1,6-C,H insertion of **3** to **5** by a factor of about 8. Although this deduction is rather limited with reference to any quantitative conclusions, it is sufficiently reliable to realize semi-quantitatively the important role 1,2-styryl migrations play in the thermal conversion of 1-phenyl-1-buten-3-yne at temperatures above 600 °C or even 550 °C^[5] in the gas phase. Apparently, the activation energy for the 1,6-C,H insertion of the cinnamylidene carbenes (here **3**, **4**, **9**, **10**) to the naphthalenes (here **5**, **6**, **11**, **12**) has to be significantly higher than that for the 1,2-styryl migration of the corresponding carbenes to the phenylbutenyne (here **1**, **2**, **7**, **8**). These facts are qualitatively summarized in the energy profile diagram (Figure 1).

Conclusions and Prospects

The reaction course depicted in Scheme 2 that qualitatively describes naphthalene formation from phenylbutenyne proceeding via cinnamylidene carbenes proved to be correct. Moreover, at 650 °C, the relative rates of partial reactions such as 1,2-D(H) and 1,2-styryl migrations as well as 1,6-C,H insertions decrease in the following order:



Consequently, their energies of activation inevitably have to increase in the reversed order. From this and in accord-

ance with previous results,^[4] one can conclude that the importance of the 1,6-C,H insertion increases with increasing temperature, while the opposite holds true for the other partial reactions.

Finally, it seems to be very plausible that the 1,2-styryl migration, first discussed as an alternative reaction by Wentrup, Zeller and co-workers^[2c] and experimentally proven by ourselves,^[5] has to be considered as the first example of a family of hitherto undiscovered 1,2-vinyl-type migrations, which are purported to take place commonly, not only in high-temperature chemistry of compounds with enyne structure fragments, but also in hydrocarbon flames

Experimental Section

General: NMR: Varian Unity 400, ¹H NMR (400 MHz, CD₃COCD₃, int. CH₃COCH₃, δ = 2.08), ²H NMR (61 MHz, CH₃COCH₃, int. CD₃COCD₃, δ = 2.08), ¹³C NMR (100 MHz, CD₃COCD₃, int., δ = 29.8 (CD₃), δ = 206.0 (C=O); inversed gated decoupling). – Analytical GC: HP 5890 Series II (FID, H₂, column: PS 255 – quartz, 25 m × 0.32 mm × 1.2 μm, 50 °C – 5 min, 10 °C/min, 200 °C – 10 min). – GC/MS: HP 5890 Series II (MSD HP 5971A – 70 eV, He; column: SE 54, 15 m × 0.20 mm × 0.25 μm, 50 °C – 5 min, 10 °C/min, 200 °C – 10 min). – GC/FT-IR: HP 5890 Series II (IRD: HP 5965 B, ν̄ = 750–4000 cm^{−1}, N₂, column: SE 30: 25 m × 0.32 mm × 1.2 μm, 50 °C – 5 min, 10 °C/min, 200 °C – 10 min).

cis/trans-[4-¹³C]-1-Phenyl-1-buten-3-yne (7): The synthesis of **7** by reaction of [¹³C]dichloromethane (Promochem, ¹³C content: 99 atom-%) with a mixture of *n*-butyllithium, cinnamyl bromide, and HMPT in diethyl ether solution at −78 °C, followed by a double dehydrohalogenation with potassium *tert*-butoxide, has already been described in detail.^[1] – *trans*-[4-¹³C]-1-Phenyl-1-buten-3-yne: MS: *m/z* (%): 130 (10), 129 (100) [M⁺], 128 (26), 127 (9), 103 (12),

102 (6), 78 (6), 63 (4). – FT-IR: $\tilde{\nu}$ = 3312 cm⁻¹ (¹³C4–H4 valence vibration), 3092, 3039, 2076, 1951, 1880, 1786, 1492, 1198, 953. – NMR: For NMR data (¹H-, ²H-, ¹³C NMR), see under “Analysis of the Pyrolyzates”.

cis/trans-[4-¹³C,4-D]-1-Phenyl-1-buten-3-yne (1): Compound **1** was synthesized by deuteration of **7** according to the procedure that we have described previously.^[1] The residue obtained following distillation was used directly for the pyrolysis experiments. The spectroscopic data were in complete agreement with those from the previously carried out synthesis. – *trans*-**1**: MS; *m/z* (%): 131 (10), 130 (100) [M⁺], 129 (26), 128 (10), 104 (11), 78 (7), 65 (4), 51 (8). – FT-IR: $\tilde{\nu}$ = 3083 cm⁻¹, 3039, 2559 (¹³C4–D4 valence vibration), 1951, 1880, 1786, 1591, 1492, 1264, 1016, 952. – NMR: See under “Analysis of the Pyrolyzates”.

Analysis of the Pyrolyzates: The compositions of the 1-phenyl-1-buten-3-yne and naphthalene isotopomer fractions were determined from the NMR spectra, which were recorded directly from the relevant liquid pyrolyzates and the molar masses of the deuterated (*m/z* = 130) and the non-deuterated (*m/z* = 129) [¹³C]phenylbutenyne and naphthalenes. The analyses were carried out on the basis of well-known ¹³C-, ¹H- and ²H-NMR data [chemical shifts δ (ppm), coupling constants *J* (Hz)] already detailed in ref.^[1] (see ref.^[9] therein), taking the intensities of the signals in the recorded spectra into account. In this way, it is possible to distinguish the *trans* as well as the *cis* configurations of **1**, **7** and **2**, **8** on the basis of the different coupling constants of the olefinic H and D atoms (H1, H2, D1, D2), respectively, with the ¹³C atoms in the C-3 and C-4 positions.

Representative relevant NMR data are listed below for the *trans*-1-phenyl-1-buten-3-yne: ¹H NMR: *trans*-**1**(**7**): H1: 7.1 (d, ³*J*_{H1,H2} = 16.4), H2: 6.4 (dd, ³*J*_{H2,H1} = 16.4, ³*J*_{H2,C4} = 4.4); *trans*-**2**(**8**): H1: 7.1 (dd, ³*J*_{H1,H2} = 16.4, ³*J*_{H1,C3} = 8.4), H2: 6.4 (dd, ³*J*_{H2,H1} = 16.4, ³*J*_{H2,C3} = 0.4). – ²H NMR: *trans*-**1**: D4: 3.4 (d, ¹*J*_{D4,C4} = 38.6); *trans*-**2**: D4: 3.4 (d, ²*J*_{D4,C3} = 7.6). – ¹³C NMR: *trans*-**1**: C4: 80.8 (t, ¹*J*_{C4,D4} = 38.6); *trans*-**2**: C3: 83.0 (t, ²*J*_{C3,D4} = 7.6); *trans*-**7**: C4: 81.1 (s); *trans*-**8**: C3: 83.5 (s).^[12]

The proportions of the *naphthalene isotopomers* were determined from the intensities of the signals of the ¹³C-labelled atoms in the ¹H-decoupled ¹³C-NMR spectra and of the D atoms in the ²H-NMR spectra (see below), taking into account the relevant mass-spectrometrically determined data.

¹³C NMR: [1-¹³C,1-D]naphthalene: C1: 128.7 (t, ¹*J*_{C1,D1} = 24.4); [2-¹³C,1-D]naphthalene: C2: 126.9 (s); **5**: C1: 128.9 (s); **6**: C2: 126.7 (t, ¹*J*_{C2,D2} = 24.4); **11**: C1: 127.0 (s); **12**: C2: 129.0(s). – ²H NMR: [1-¹³C,1-D]naphthalene: D1: 7.9 (d, ¹*J*_{D1,C1} = 24.4); [2-¹³C,1-D]naphthalene: D1: 7.9 (s); **5**: D2: 7.5 (s); **6**: 7.5 (d, ¹*J*_{D2,C2} = 24.4).

Pyrolysis: The pyrolyses were carried out as already described elsewhere^[2c] by passing the starting materials together with nitrogen or a nitrogen/toluene mixture as diluent gas at a given temperature through a quartz tube, which was placed in an electrical heating system. The tube was connected to a cold trap (–195.8°C), in which the liquid pyrolyzates were collected. After warming to ambient temperature, the pyrolyzates were analyzed by analytical gas chromatography, GC/MS analysis, and NMR spectroscopy as described previously.^[1] The phenylbutenyne was introduced into the reactor as 0.7–0.9-mL samples of a 10% solution in benzene.

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