Addition and Cyclization Reactions in the Thermal Conversion of Hydrocarbons with an Enyne Structure, 6[◇]

Naphthalene Isotopomers from Isotope-Labelled Phenyl-Annelated 1,3-Hexadien-5-ynes Facilitate an Evaluation of Competing Radical Cycloisomerization Pathways☆

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The thermal cycloisomerization of the isotope-labelled 1-phenyl-1-buten-3-ynes **1** {including the [3-^{13}C,4-D]1-phenyl-1-buten-3-yne (**6**) and the [4-D]1-phenyl-1-buten-3-yne (**9**) formed as intermediates} has been studied. The investigations were performed in a quartz flow system at a temperature of 650 °C (**1**, **6**) [and over the range 625–750 °C for (**9**)] at a reaction time of 0.3 s in the presence of different diluent gases (H_2, N_2, N_2–toluene). Spectroscopic analyses of the naphthalene isotopomers formed allow the evaluation of competing radical reaction channels in addition to reactions occuring by electrocyclic and carbene-like ring closure.[1] A mechanistic analysis for the conversion of **1** undoubtedly suggests a predominant reaction course via phenyl-type radical intermediates (**1c**/**6c**), followed by their exocyclization to the indenylcarbenyl radicals **1f**/**6f** and the homoallyl-like rearrangement of the latter to the 1,2-dihydronaphthyl radicals **1i**/**6i** at 650 °C. With increasing temperature, other competing reactions (endocyclizations of vinyl- and phenyl-type radicals as well as neophyl-like rearrangements of the indenylcarbinyl radicals **1f**/**6f**) gain in importance.

For many years the cyclization of 1,3-hexadien-5-ynes, first reported by Hopf and Musso[2] in 1969, has been of secondary importance when compared with the Bergman cyclization of 1,5-hexadiyn-3-enes[3]. During the last decade, however, several 1,3-hexadien-5-ynes have turned out to be useful precursors in the high-temperature synthesis of planar[4] and bowl-shaped polycyclic aromatics,[5] as well as a new family of compounds with an exotic architecture.[6] Moreover, recently published results support the notion that at temperatures above 600°C, 1,3-hexadien-5-ynes are obviously able to cyclize alkenylidene carbenes, and vinyl-type radicals in parallel via isoaromatics.[1][4c] While the mechanisms of the formation of aromatic ring systems from 1,3-hexadiene-5-ynes via isoaromatics and alkenylidene carbenes can easily be understood on the basis of well-documented precedent reactions, the significance of competing radical reaction cascades[4c] cannot be assessed easily. An evaluation of the different radical pathways other than unimolecular cyclizations initiated by electrocyclization and alkenylidene carbenes requires experiments with isotope-labelled 1,3-hexadien-5-ynes.

For this purpose, the formation of the naphthalene isotopomers from [4-^{13}C,4-D]1-phenyl-1-buten-3-yne (**1**) has been studied at 650°C. The analysis made use of the ability of **1** to autoisomerize into the [3-^{13}C,4-D]1-phenyl-1-buten-3-yne (**6**) by 1,2-D and 1,2-styryl migration.[7] Additional studies of the conversion of [4-D]1-phenyl-1-buten-3-yne (**9**) between 650 and 750°C were finally carried out to determine the temperature dependence of the competing radical reaction cascades experimentally.

Results

Thermal Conversion of [4-^{13}C,4-D]1-phenyl-1-buten-3-yne (1)

[4-^{13}C,4-D]1-Phenyl-1-buten-3-yne (**1**) was prepared in a three-step synthesis using conditions guaranteeing high yields of **1** baseded on [^{13}C]dichloromethane (Scheme 1). The starting compound **1** was obtained as a 1:99 *cis/trans* mixture (yield: 38%, based on [^{13}C]dichloromethane). The GC purity amounted to 98.6%, the D and ^{13}C content to 99 atom-% each (see Experimental Section). The hydrocarbon served directly as feedstock for the pyrolysis runs as a 10%

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solution in benzene. In each run, 0.8 ml of the solution of **1** was slowly evaporated into either a stream of nitrogen (N_2), a nitrogen−toluene mixture (N_2−tol), or hydrogen (H_2), respectively. These gases served as diluents (= dg) carrying **1** in low concentrations ($n_{dg}/n_{\mathbf{1}} \approx 50{:}1$) at 650°C (0.3 s) through a tubular quartz reactor described elsewhere.[1] The liquid pyrolyzates were collected in a cold trap (cf. for example ref.[1][4c]), dissolved in 1 ml of acetone (see Experimental Section), and analyzed (GC, GC/MS, GC/FT-IR, ^{1}H, ^{2}H and ^{13}C NMR).[7][8][9] The yields of the liquid pyrolyzates (unconverted **1**, benzene, products) always amounted to more than 95% of the employed solutions. The degree of conversion and the composition of the products formed depended on the nature of the diluent gas used. The numerical values listed in Table 1 agree with those obtained recently from the thermal conversion of unlabelled 1-phenyl-1-buten-3-yne under comparable conditions.[4e] All pyrolyzates consisted of the naphthalene isotopomers **2** to **5**, **7** and **8**, 1-methylene-1*H*-indenes and azulenes as well as unconverted **1** and its automerization product **6** (Scheme 2). The concentrations of **1** and **6** were determined by ^{1}H and ^{13}C NMR as well as by GC/FT-IR analysis following the instructions and using the data reported in ref.[7] The determination of the molar portions of the naphthalene isotopomers **2**−**5**, **7** and **8** in the pyrolyzates was carried out by ^{13}C-NMR spectroscopy in view of the characteristic spectroscopic data of these isotopomers reported in ref.[9] (see also Experimental Section). The determined molar portions of **2**−**5**, **7** and **8** in the pyrolyzates of **1** obtained at 650°C (0.3 s) in the presence of N_2−tol, N_2 and H_2, respectively, are depicted in Figure 1; they correspond to the yields of naphthalene formed from unlabelled 1-phenyl-1-buten-3-yne and amount to 8% (N_2−tol), 16% (N_2), and 25% (H_2).

Scheme 1

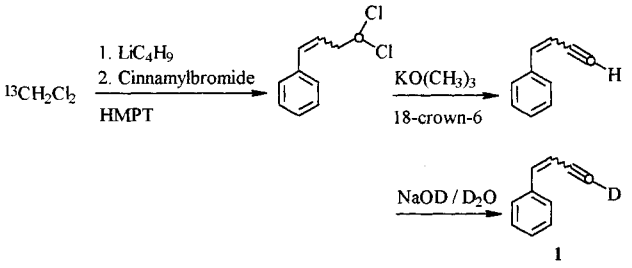
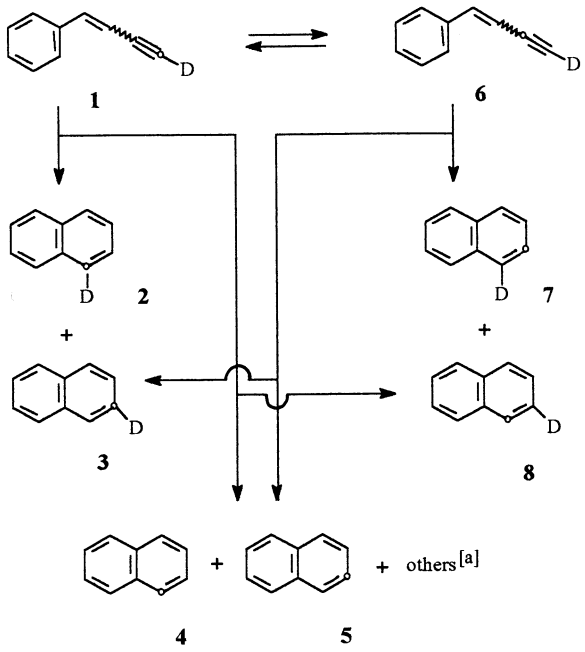


Table 1. Dependence of the conversions and product selectivities S[a] in the pyrolysis of **1** on the carrier gas used (650°C, 0.3 s)

Carrier gas	N_2−tol[b]	N_2	H_2
Conversion [%]	8	16	25
Products [*S*]			
[^{13}C,D]naphthalenes	96	87	86
[^{13}C,D]1-methylene-1*H*-indenes	–	11	11
[^{13}C,D]azulenes	3	1	1
others	1	1	2

[a] S = product moles formed from 100 moles of the starting compound converted. − [b] 5 mol-% toluene in nitrogen.

Scheme 2

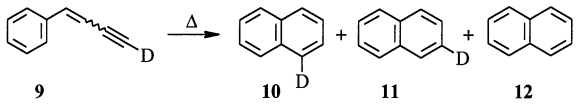


[a] Minor isotopomers of 1-methylene-1*H*-indene and azulene.

Temperature Dependence of the Products Formed from [4-D]1-phenylbut-1-en-3-yne (9)

The deuterated phenylbutenyne **9** was prepared and pyrolyzed and the pyrolyzates were analyzed as described in ref.[1] To determine the temperature dependence of the main products formed (Scheme 3), **9** was converted between 650 and 750°C in N_2−tol and N_2 at each temperature. Table 2 lists the conversions and the pyrolyzate compositions in an abridged version.

Scheme 3



Thermal Conversion of the [4-^{13}C]1-phenyl-1-buten-3-yne

[4-^{13}C]1-phenylbut-1-en-3-yne was available as an intermediate in the synthesis of **1** before the H/D exchange was carried out. It was pyrolyzed at 650°C in the presence of N_2 as described above for compound **1**. The conversion of [4-^{13}C]1-phenyl-1-buten-3-yne (18%) and the proportions of the [1-^{13}C]- (**4**) and [2-^{13}C]naphthalene (**5**) formed in the pyrolyzates amounted to 54 and 46 mol-%, which is consistent with the expected ^{13}C distribution in the naphthalene isotopomer fraction obtained in the corresponding pyrolysis of **1**.

Table 2. Temperature dependence of the products formed from **9** in presence of N_2−tol and N_2 at 650, 700 and 750°C (yields in selectivity units[a])

Temperature [°C]	650		700		750	
Diluent gas	N_2−tol[b]	N_2	N_2−tol[b]	N_2	N_2−tol[b]	N_2
Conversion [%]	8	18	25	42	56	82
Products [*S*]						
[1-D]naphthalene **10**	12	15	12	15	11	16
[2-D]naphthalene **11**	78	62	79	64	80	64
naphthalene **12**	8	13	4	9	2	8
1-methylene-*1H*-indenes[c]	–	9	tr.	8	1	7
azulenes[d]	2	1	3	1	4	1
others	tr.	tr.	1	1	1	1

[a] *S* = product moles formed from 100 moles of the converted substrate. – [b] 5 mol-% of toluene in nitrogen. – [c] Deuterated and undeuterated methylene-1*H*-indenes. – [d] Deuterated and undeuterated azulenes.

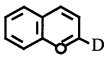
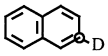
Discussion

General

Diluent gases of different nature change the molar percentages of the naphthalene isotopomers formed in the pyrolysis of **1** (see Table 3 and Figure 1). Such changes may be traced back to the different steady-state concentrations of chain-carrier radicals, which are thought to be the result of consecutive reactions of the radicals formed primarily from the thermal decomposition of **1**, with hydrogen [according to $R^{\bullet} + H_2 \rightleftarrows RH + H^{\bullet}$ when H_2 is used as diluent) or with toluene [according to $R^{\bullet}$ ($H^{\bullet}$) + Ph−CH_3 $\rightleftarrows$ RH (H_2) + Ph−CH_2· when **1** is converted in the presence of N_2−tol mixtures].[1] Referring to the results obtained in N_2, the steady-state concentrations of the most reactive chain-carrier radicals ($H^{\bullet}$) increase in H_2, while they decrease in N_2−tol, because reactive radicals cause the formation of less reactive benzyl radicals. The dependences of the molar percentages of the naphthalene isotopomers **2**−**5**, **7** and **8** follow indirectly from the results displayed in Figure 1. The increase of the molar percentages is connected with the increase of the radical conversion of **1** (Table 3) which is initiated by radical reactions such as the ones depicted in Scheme 4, as well as by the radicals formed from **6** (see Scheme 5). This effect occurs because the portions of the naphthalene isotopomers (formed by molecule-induced or electrocyclic ring closures and by 1,6-C,H insertions of alkenylidene carbenes formed as intermediates[1][4d]) proceed independently of the kind of the diluent. A comparison of the increases of the individual isotopomers **2**−**5**, **7** and **8** clearly reveals that **3** is mostly favoured by changing the diluent from N_2−tol via N_2 to H_2. Following the reaction cascades depicted in Scheme 4 and their counterparts for **6** (cf. Scheme 5), **3** is only formed by radicals from **1** by the reaction cascade involving the intermediates **1c** → **1f** → **1h** → **1i** and the homoallyl-like rearrangement of **1f** to **1i**. Thus, the phenyl-like radicals **1c** (and **6c**) may be assumed to act as key intermediates in the radical reaction cluster considered.

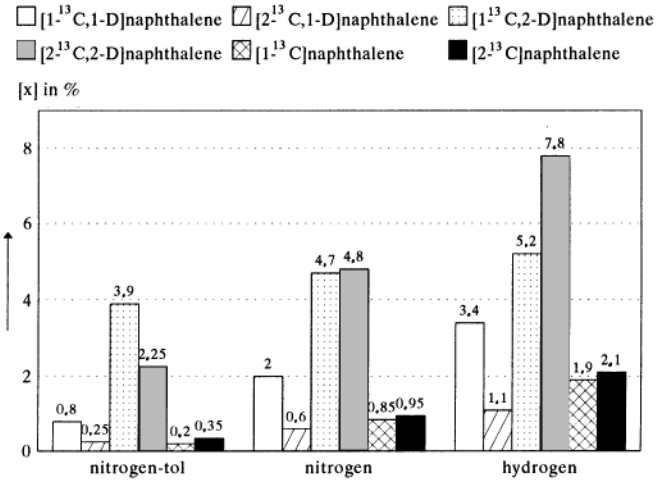
The naphthalene **2** is an additional isotopomer, which is presumably formed exclusively from **1**. It is formed in parallel via two different intermediates, the vinyl-type radical **1a** and the phenyl-type radical **1c**. The corresponding increase of the molar percentage is, however, smaller than that of **3**, from which we conclude that the reaction cascade representing the formation of **3** is more favoured at 650°C than the sums of the competing cascades ending in **2**. A comparison of the increase of the molar percentage of **8** and **7** does not contradict the above statement. The difference between the increase is, however, less pronounced. This is thought to be caused by falsification resulting from large portions of **8** formed in parallel by the corresponding alkenylidene carbene route (Scheme 6).[1] Although the preceding assertions are only of qualitative nature, analogous discussions are not possible for the formation of the nondeuterated ^{13}C-naphthalenes **4** and **5**. Both compounds can in principle be formed from the intermediates **1e**/**6e** and **1i**/**6i** by β(C−D) bond scission as well as by radical dedeuteration of the [^{13}C,D]naphthalenes **2**, **3**, **7**, and **8** already formed. In reference experiments in which we treated [1-D]-(**10**) and [2-D]naphthalene (**11**) at 650°C (0.3 s) and otherwise comparable conditions, it was seen that both com-

Table 3. Listing of the molar percentage [**x**] of **2**−**5**, **7**, and **8** determined in the pyrolyzates from **1** (650°C, 0.3 s) in the presence of N_2−tol and N_2, the differences between the corresponding molar percentages obtained in N_2 and N_2−tol ([**x**]), and the molar percentages for the radical routes ($[\mathbf{x}]_{rad}$)[a].

Isotopomers	x	$[\mathbf{x}]_{N_2}$	$[\mathbf{x}]_{N_2-tol}$	$\Delta[\mathbf{x}]$[b]	$[\mathbf{x}]_{rad,N_2}$	$[\mathbf{x}]_{rad,N_2-tol}$
	**2**	2	0.8	1.2	1.7	0.5
	**7**	0.6	0.25	0.35	0.5	0.15
	**8**	4.7	3.9	0.8	1.1	0.3
	**3**	4.8	2.25	2.55	3.5	0.95
	**4**	0.85	0.2	0.65	0.85	0.25
	**5**	0.95	0.25	0.7	0.95	0.25

[a] Calculated in accordance with eq. 1. – [b] $\Delta[\mathbf{x}] = [\mathbf{x}]_{N_2} - [\mathbf{x}]_{N_2-tol}$.

Figure 1. Molar percentages of the naphthalene **2**−**5**, **7**, and **8** in the pyrolyzates of **1** (650°C, 0.3 s) in the presence of N_2−tol,[a] N_2, and H_2, respectively[b]



[a] 5 mol-% toluene in nitrogen. − [b] 2 mol-% of **1** in the corresponding diluent gas.

pounds do not lose deuterium significantly. The only important precursors for the formation of **4** and **5** must therefore be considered to be the corresponding dihydronaphthyl radicals **1i**, **1e**, **6i** and **6e**.

For a more detailed and quantitative interpretation of the complicated reaction cluster by numerical evaluation in view of the fact that H/D isotope effects cannot be neglected.

Numerical Evaluation of Competing Radical Reaction Channels

According to ref.[1], the differences Δ[**x**] between the spectroscopically determined molar percentages [**x**] in which the naphthalene isotopomers **2**−**5**, **7**, and **8** are available in the pyrolyzates (Table 3) when **1** is thermally converted in the presence of N_2−tol ($[\mathbf{x}]_{N_2-tol}$) and in N_2 ($[\mathbf{x}]_{N_2}$), respectively, represent the portions formed by radicals in each case, and apply

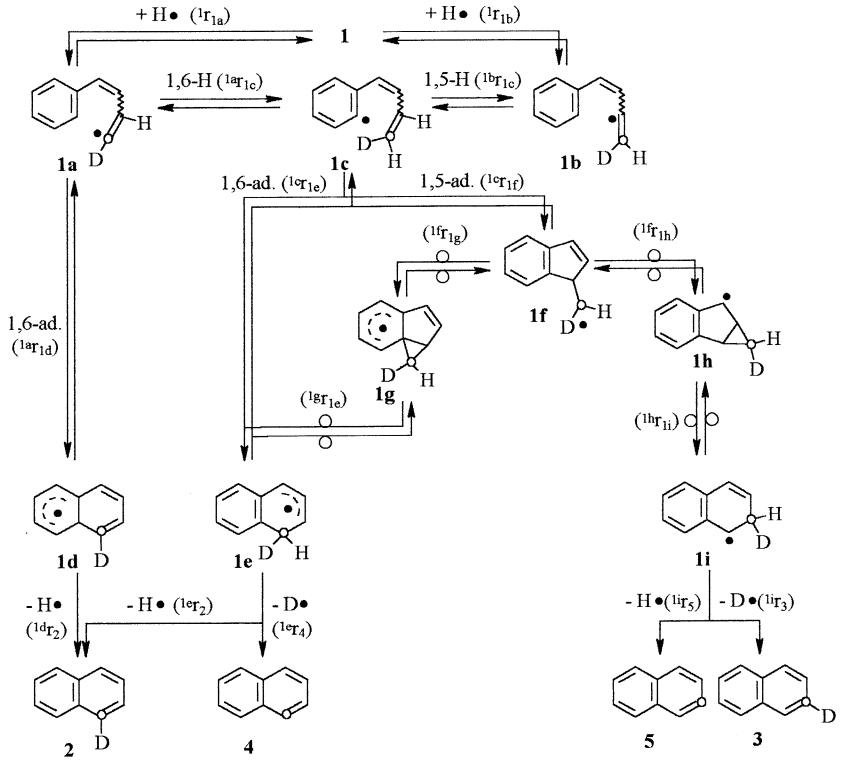
$$\Delta[\mathbf{2}]:\Delta[\mathbf{3}]:\Delta[\mathbf{4}]:\Delta[\mathbf{5}]:\Delta[\mathbf{7}]:\Delta[\mathbf{8}] = [\mathbf{2}]_{rad}:[\mathbf{3}]_{rad}:[\mathbf{4}]_{rad}:[\mathbf{5}]_{rad}:[\mathbf{7}]_{rad}:[\mathbf{8}]_{rad} \quad (1)$$

4 and **5** are exclusively formed by radical reactions ([**4**] = $[\mathbf{4}]_{rad}$, [**5**] = $[\mathbf{5}]_{rad}$), and Eq. 1 therefore makes it possible to calculate the molar percentages in which **2**, **3**, **7** and **8** are formed via radical intermediates in each run (Table 3, column 4 and 5).

Consequently, the reaction sequence from **1c**/**6c** via **1f**/**6f** and finally **1i**/**6i** to **3**/**8** (cf. for example Scheme 4) on the one hand and the sum of the parallel sequences operating **1a**/**6a** → **1d**/**6d**, **1c**/**6c** → **1e**/**6e** (including the sequence **1c**/**6c** → **1f**/**6f** → **1g**/**6g** → **1e**/**6e**) on the other, finally result in the **2**/**7** ratio. Both reaction courses are clearly quantifiable. **4** and **5** are formed simultaneously from **1**, as well as from **6** in the opposite sense, and thus the weighting of the distinguishable, competing reaction events requires the knowledge of the ratio of the steady-state concentrations in which **1** and **6** become effective in the reactor (R_{eff}).

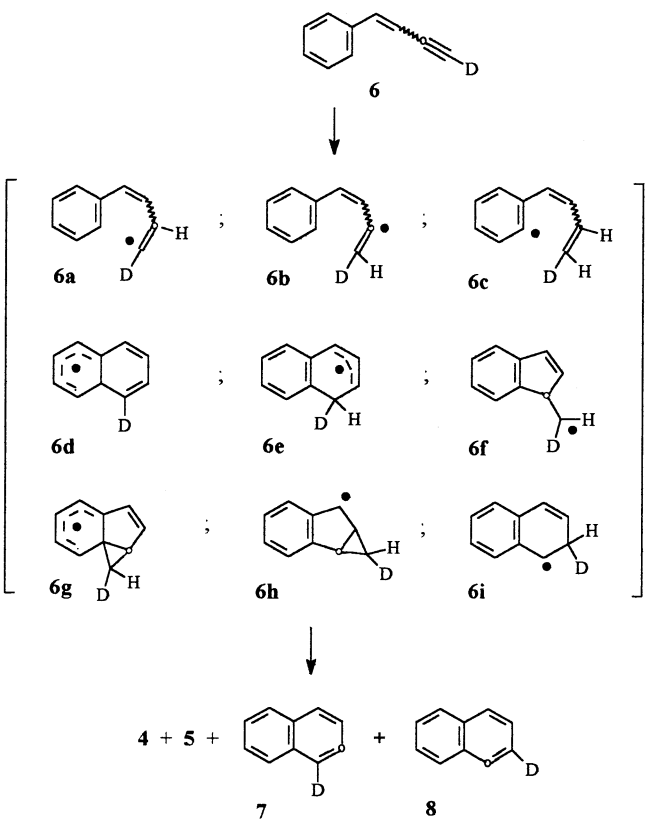
Assuming the reactor used operates as an ideal plug-flow system, the corresponding calculations[11] result in **1**/**6** dis-

Scheme 4

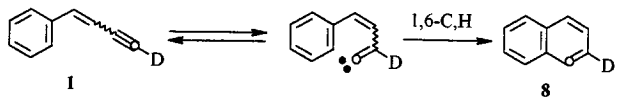


o = ^{13}C and $^{i}r_{j}$ denoting the reaction from species **i** to **j**.

Scheme 5

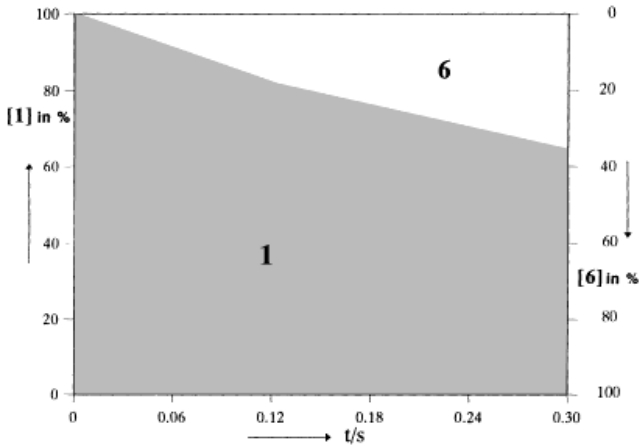


Scheme 6



tributions along the reactor axis (corresponding to the reaction time, τ) as displayed in Figure 2. The time course of the curve reveals that at 650°C, products from **6** might have only a small influence on the composition of the naphthalene isotopomers.

Figure 2. Dependence of the average percentage of **1** and **6** on the residence time in the reactor (650°C, no carrier gas at all)



Confirmation of this assumption is furnished by the calculation of R_{eff} from **2** (exclusively formed from **1**) and **7** (from **6**) by $[\mathbf{2}]_{rad}/[\mathbf{7}]_{rad} \approx 3.3$ [which is completely consistent with the value obtained from the radical production of **3** (from **1**) and **8** (from **6**)]. The molar percentages of **4** and **5**, formed by the different reaction cascades, are calculable from the R_{eff} value, using the Eq. 2 to 5, in which the superscripted indices indicate the reaction steps depicted in Scheme 4 (and for the corresponding equivalents when the reaction cluster is started from **6**, Scheme 5)

$$[\mathbf{4}]^{(^{1c}r_{1e}\rightarrow{}^{1e}r_4)} + [\mathbf{4}]^{(^{1c}r_{1f}\rightarrow\ldots\rightarrow{}^{1e}r_4)} = R_{eff}\left[[\mathbf{5}]^{(^{6c}r_{6e}\rightarrow{}^{6e}r_5)} + [\mathbf{5}]^{(^{6c}r_{6f}\rightarrow\ldots\rightarrow{}^{6e}r_5)}\right] \quad (2)$$

$$[\mathbf{5}]^{(^{1f}r_{1h}\rightarrow\ldots\rightarrow{}^{1i}r_5)} = R_{eff}[\mathbf{4}]^{(^{6f}r_{6h}\rightarrow\ldots\rightarrow{}^{6i}r_4)} \quad (3)$$

which finally end in the following solutions.[12]

$$[\mathbf{5}]^{(^{6c}r_{6e}\rightarrow{}^{6e}r_5)} + [\mathbf{5}]^{(^{6c}r_{6f}\rightarrow\ldots\rightarrow{}^{6e}r_5)} = \frac{[\mathbf{5}] - R_{eff}[\mathbf{4}]}{1 - R_{eff}^{\,2}} \quad (4)$$

$$[\mathbf{4}]^{(^{6f}r_{6h}\rightarrow\ldots\rightarrow{}^{6i}r_4)} = \frac{[\mathbf{4}] - R_{eff}[\mathbf{5}]}{1 - R_{eff}^{\,2}} \quad (5)$$

The calculated molar percentages of **4** and **5**, formed in competing reactions from the phenyl-type radicals **1c** and **6c** in the presence of N_2 and N_2−tol, respectively, are listed in Table 4. The molar percentages (Tables 3 and 4) in which the individual naphthalene isotopomers are formed by different reaction cascades make an evaluation possible, because the competing radical reactions are distinguishable. The results are shown in Table 5 in which indistinguishable reactions are partly combined together. They reveal unambiguously that phenyl-type intermediates such as **1c** and **6c** play a dominant role. In addition, they show that the exocyclization of such phenyl radicals[13] followed by a homoallyl-like rearrangement of intermediates such as **1f** and **6f** to **1i** and **6i** controls approximately 65% of those radical reactions which convert **1** and **6** into the naphthalene isotopomers **3** to **5** and **8**, even at 650°C. The remaining 35% of the radical reaction cluster is apportioned to three further competing reaction cascades including those such as the endocyclization of **1a**/**6a** to **1d**/**6d**, of **1c**/**6c** to **1e**/**6e** and the exocyclization of **1c**/**6c** to **1f**/**6f**, followed by their neophyl-like rearrangements[10] to **1g**/**6g** (cf. for example ref.[14]).

Table 4. Molar percentages in which **4** and **5** are formed from the phenyl-type radicals **1c** and **6c** in competing reactions

[^{13}C]naphthalenes **x**	reaction routes[a]	molar percentages [**x**] in the presence of N_2	N_2−tol
4	$(^{1c}r_{1e} \rightarrow {}^{1e}r_4) + (^{1c}r_{1f} \rightarrow\ldots\rightarrow {}^{1e}r_4)$	0.6	0.2
4	$(^{6c}r_{6f} \rightarrow\ldots\rightarrow {}^{6i}r_4)$	0.2	0.1
5	$(^{6c}r_{6e} \rightarrow {}^{6e}r_5) + (^{6c}r_{6f} \rightarrow\ldots\rightarrow {}^{6e}r_5)$	0.2	0.1
5	$(^{1f}r_{1h} \rightarrow\ldots\rightarrow {}^{1i}r_5)$	0.8	0.2

[a] For the symbols used see Schemes 4 and 5.

Table 5. Molar percentages of experimentally distinguishable radical reactions in the formation of the isotopomers **2**−**5**, **7** and **8** from **1**/**6** on pyrolyzing **1** in nitrogen at 650°C

Sequences[a]	Route	Products	Molar percentages[b] from **1**	from **6**	total
...→ **1c/6c** → **1f/6f** → **1h/6h** → **1i/6i**					
1i/6i	− H•→	**3** + **8**	3.5	1.06	4.56
1i/6i	− D•→	**4** + **5**	0.8	0.25	1.05
Σ(...→ **1a/6a** → **1d/6d** + ...→ **1c/6c** → **1e/6e** + ...→ **1c/6c** → **1f/6f** → **1g/6g** → **1e/6e**)					
1d/6d + **1e/6e**	− H•→	**3** + **8**	1.7	0.5	2.2
1e/6e	− D•→	**4** + **5**	0.6	0.8	0.8

[a] For the symbols used see Schemes 4 and 5. − [b] Referring to the pyrolyzates.

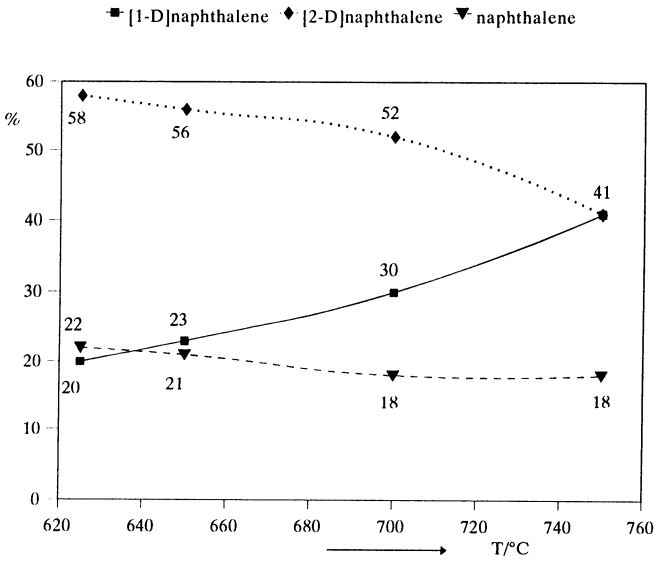
Finally, the formation of **3** and **5** (from **1**) as well as of **4** and **8** (from **6**) involves β(C−H) and β(C−D) cleavages of the corresponding 1,2-dihydronaphthyl radicals **1i** and **6i**, respectively. Ignoring the negligible $^{12}C/^{13}C$ isotope effect, this indicates an H/D isotope effect for the pathway via "benzyl-type" radicals **1i**/**6i** of approximately 4.5. This is considerably smaller than the H/D isotope effect for the pathway involving the "allyl-type" radicals **1e**/**6e** calculated to be at most 2.8, when the channel from **1a**/**6a** via **1d**/**6d** to **2**/**7** is assumed to be inoperative. This assumption, however, is not valid and so the actual value is assumed to be smaller than 2.8.

Temperature Dependence of the Competing Radical Reaction Channels to the Naphthalenes

It is known from our very recently published paper[1] that the radical reactions from 1-phenyl-1-buten-3-ynes to the corresponding naphthalenes lose importance with increasing temperature in favour of 1,6-C,H insertions of alkenylidene carbenes which are formed as intermediates. As expected, changes such as that should also be accompanied by changes in the relative importance of the competing radical reactions themselves. Figure 3 displays the calculated temperature dependence of the naphthalenes **10** to **12** formed by radicals during the pyrolysis of [1-D]1-phenyl-1-buten-3-yne (**9**) in nitrogen (see also Table 2). It shows that the molar percentage of the [2-D]naphthalene (**11**) in the corresponding naphthalene fraction decreases with increasing temperature from 58% at 625°C to 41% at 750°C. A similar plot applies for the formation of the nondeuterated naphthalene **12**, although at a distinctly lower level (from 22 to 18%). In contrast, the plot for [1-D]naphthalene (**10**) increases while **11** grows, actually from 20 to 41%.

Taking these results as the basis for the mechanistic analysis of the formation of the naphthalene isotopomers from **1**/**6**, one can clearly conclude that the radical reactions from **1** to **2** and **4** as well as from **6** to **5** and **7** gain increasing importance with increasing temperature. Thus, the radical events are obviously dominated by pathways which ter-

Figure 3. Temperature dependence of the darically formed naphthalenes **10**−**12** (= 100%) from **9** in the pyrolyzates (nitrogen, 0.3 s)



minate the reactions of **1a**/**6a** to **1d**/**6d** and of **1c**/**6c** to **1e**/**6e**. Moreover, there is every reason to assume that the endocyclization of the vinyl-type radicals **1a**/**6a** is accelerated stronger than that of the vinyl-type radicals **1c**/**6c**. We consider this a logical consequence of the observation that the portion of **10** formed by a radical route increases with increasing temperature to a significantly higher extent than that of **12**.

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Experimental Section

General: NMR: Varian-Unity 400, ^1H NMR (400 MHz, CD_3COCD_3, int. CH_3COCH_3, δ = 2.08), ^2H NMR (61 MHz, CH_3COCH_3, int. CD_3COCD_3, δ = 2.08), ^{13}C NMR [100 MHz, CD_3COCD_3, int., δ = 29.8 (CD_3), δ = 206.0 (C=O); inverse gated decoupling]. − GC, analytical: HP 5890 Series II (FID, H_2, col-

umn: 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/FTIR: HP 5890 Series II, IRD HP 5965 B, $\tilde{\nu}$ = 750−4000 cm^{-1}, N_2, 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-^{13}C]1-Phenyl-1-butene-3-yne: Synthesized according to ref.[8]: A 1.6 M solution of *n*-butyllithium in *n*-hexane (14 ml), diethyl ether (60 ml) and THF (30 ml) was placed in a flask equipped with a stirrer, a dropping funnel, a low-temperature thermometer, and a nitrogen inlet tube. ^{13}C-dichloromethane (PROMOCHEM, ^{13}C content: 99 atom-%) was added dropwise under stirring for 40 min at − 78°C, a solution of *trans*-cinnamyl bromide (4.57 g; 23.2 mmol) in 10 ml THF introduced, and a 1:1 mixture of THF and HMPT added at −90°C. After 30 min, the mixture was allowed to reach −85°C (20 min). Sulfuric acid (40 ml, 4 N) was rapidly introduced, the organic layer was separated, extracted with ether (3 × 50 ml), washed with a saturated solution of sodium chloride (100 ml), dried with magnesium sulfate, and the solvent removed by distillation at reduced pressure (0.2 bar, yield: 70% [4-^{13}C]4,4-dichloro-1-phenyl-1-butene and 6% [1-^{13}C]1-chloro-4-phenylbuta-1,3-diene). The mixture was used directly for the dehydrohalogenation. − *trans*-[4-^{13}C]4,4-dichloro-1-phenylbut-1-ene: MS; *m/z* (%): 203(9), 201(13) [M^+], 130(9), 129(12), 118(11), 117(100), 116(9), 115(30), 91(12), 77(6), 51(9). − The product mixture was dissolved in *n*-hexane (100 ml) and placed in a flask (equipped with stirrer, dropping funnel, low-temperature thermometer, and nitrogen inlet tube), and 15 mg of 18-crown-6 and 10.1 g (90 mmol) of potassium *tert*-butoxide was added under intensive cooling. The mixture was stirred for 3 h, while the temperature increased to 60°C. Sulfuric acid (40 ml, 4 N) was added dropwise at −60°C, the organic layer was separated, the inorganic layer extracted with *n*-hexane (3 × 50 ml), the mixed organic layers washed with saturated sodium chloride and then dried with magnesium sulfate. The solvent was removed by distillation and the residual raw product purified by column chromatography with hexane (adsorbent: LiChroprep Si 100, Merck, yield: 40%, ^{13}C content: 99 atom-% at C-4). − *trans*-[4-^{13}C]1-Phenyl-1-butene-3-yne: MS; *m/z*(%): 130(10), 129(100) [M^+], 128(26), 127(9), 103(12), 102(6), 78(6), 63(4). − IR(FT-IR): $\tilde{\nu}$ = 3313 cm^{-1}, 3092, 3039, 2076, 1951, 1880, 1786, 1492, 1198, 953.

cis/trans-[4-^{13}C,4-D]1-Phenyl-1-butene-3-yne (**1**): Compound **1** was synthesized by deuteration of [4-^{13}C]1-phenyl-1-buten-3-yne according to the procedure previously described for the deuteration of 1-phenyl-1,3-hexadien-5-yne.[4d] 2.56 g (20 mmol) of [4-^{13}C]1-phenyl-1-buten-3-yne was dissolved in 5 ml of benzene, added to 0.8 ml of a 30% NaOD solution in D_2O and the mixture was stirred for 24 h at room temperature. After neutralization with DCl, the organic layer was separated. The procedure (starting with the addition of the NaOD solution) was repeated twice. The mixed organic layers were dried with magnesium sulfate and the solvent benzene removed by distillation. The residue [a 1:99 *cis/trans* mixture of **1**, yield 2.51 mg (38% referring to ^{13}C-dichloromethane), D content: 99 atom-%, ^{13}C content: 99 atom-% at C-4] served directly for the pyrolysis experiments without any further purification. − *trans*-**1**: MS; *m/z* (%): 131(10), 130(100) [M^+], 129(26), 128(10), 104(11), 78(7), 65(4), 51(8). − IR(FT-IR): $\tilde{\nu}$ = 3083 cm^{-1}, 3039, 2559, 1951, 1880, 1786, 1591, 1492, 1264, 1016, 952.

cis/trans-1-Phenyl-1-butene-3-yne: Synthesized by desilylation of *cis/trans*-1-phenyl-4-(trimethylsilyl)-1-butene-3-yne and separated/purified as recently described.[1] Yield and purity correspond with the data reported there.

cis/trans-[4D]1-Phenyl-1-butene-3-yne (**9**): The synthesis was carried out according to ref.[4d] by deuteration of *cis/trans*-1-phenyl-1-butene-3-yne. The GC/MS and GC/FT-IR data of **9** are identical with those listed there.

Other Spectroscopic Data: The ^{13}C-NMR data of the ^{13}C-labelled naphthalenes **2**, **3**, **4**, **5**, **7**, **8**, and of the labelled 1-phenyl-1-butene-3-ynes are given in ref.[9].

Pyrolysis: The pyrolyses were carried out in the presence of oxygen-free diluent gases [nitrogen, and molar mixtures of nitrogen−toluene (ca. 20:1)] by using a tubular flow reactor as previously described (quartz, D_i: 10 mm, *L*: 300 mm, electrically heated)[1]. The labelled 1-phenylbut-1-ene-3-ynes were introduced as 10% mixtures in benzene by syringe into a thermostated vaporizer filled with quartz wool at the upper part of the set-up. The vaporizer served to bring the carrier gas and the starting mixture to a temperature which guaranteed loading of the gas stream with approximately 2% of the substrate mixture. The reaction time was 0.3 s and the temperature varied between 625 and 750°C. After leaving the reactor, the hot effluent was rapidly cooled down with liquid nitrogen. The liquid products were collected in a trap and analyzed by GC/MS and GC/FT-IR, ^{13}C-, ^{2}H- and ^{1}H-NMR spectroscopy.

☆ Dedicated to Professor *W. Pritzkow*, Merseburg, on the occasion of his 70th birthday.

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[9] NMR shifts (δ values) and coupling constants [Hz]: *4[D]1-phenyl-1-buten-3-ynes* (phenylic C atoms): 1′: 136.7; 2′ and 6′: 127.0; 3′ and 5′: 129.4; 4′: 130.5; [4-^{13}C,4D]1-phenyl-1-buten-3-yne (**1**, C atoms of the 1-buten-3-yne fragment): *cis*-**1**: 1: 143.4; 2: 107.0 ($^2J_{C2,C4}$ = 11.6); 3: n.d.; 4: 85.9 ($^1J_{C4,D4}$ = 38.6; $^3J_{C4,H2}$ = 4.8); *trans*-**1**: 1: 143.4; 2: 108.0 ($^2J_{C2,C4}$ = 12.4); 3: 83.3 ($^1J_{C3,C4}$ = 174.0; $^3J_{C3,D4}$ = 10.0); 4: 80.8 ($^1J_{C4,D4}$ = 38.6; $^3J_{C4,H2}$ = 4.4); [3-^{13}C,4D]1-phenyl-1-buten-3-yne (**6**, C atoms of the 1-buten-3-yne fragment): *cis*-**6**: 1: 143.4; 2: 107.0 ($^1J_{C2,C3}$ = 88.3); 3: 82.0 ($^2J_{C3,D4}$ = 7.6; $^3J_{C3,H1}$ = 15.3); 4: 80.3 ($^1J_{C3,C4}$ = 173.0; $^1J_{C4,D4}$ = 38.6; $^3J_{C4,H2}$ < 0.4); *trans*-**6**: 1: 143.4; 2: 108.0 ($^1J_{C2,C3}$ = 89.8); 3: 83.0 ($^2J_{C3,D4}$ = 7.6; $^3J_{C3,H1}$ = 8.4; $^2J_{C3,H2}$ = 0.4); 4: 80.3 ($^1J_{C3,C4}$ = 174.0; $^1J_{C4,D4}$ = 38.6); *Naphthalenes* **2**−**8**: ^{13}C: **2**: 128.7 (t); **7**: 128.9 (s); **3**: 126.7 (t); **8**: 126.9 (s); **4**: 129.0 (s); **5**: 127.0 (s). − ^{2}H: **2**: 7.9 (d, $^1J_{C,D}$ = 24.4), **7** 7.5 (s); **3**: 7.5 (d, $^1J_{C,D}$ = 24.4); **8**: 7.9 (s).

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[11] The calculations were carried out by using the following equations with the simplified assumption that the autoisomerization **1** ⇌ **6** takes place exclusively

$$[\mathbf{1}]_{stat.} = \int_0^{[\mathbf{1}]} d[\mathbf{1}] = [\mathbf{1}]_{eq} \int_0^{\tau} t\, dt + ([\mathbf{1}]_0 - [\mathbf{1}]_{eq}) \int_0^{\tau} e^{-2k_i t}\, dt$$

$$[\mathbf{6}]_{stat.} = \int_0^{[\mathbf{6}]} d[\mathbf{6}] = 100\% \int_0^{\tau} dt - \int_0^{[\mathbf{1}]} d[\mathbf{1}]$$

For more details see ref.[8].

[12] For the derivatives see appendix 5 in ref.[8].

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