Addition and Cyclization Reactions in the Thermal Conversion of Hydrocarbons with an Enyne Structure, 4[◇]

Formation and Rearrangements of Bicyclic $C_{10}H_8$ Aromatics from 1-Phenyl-1-buten-3-yne

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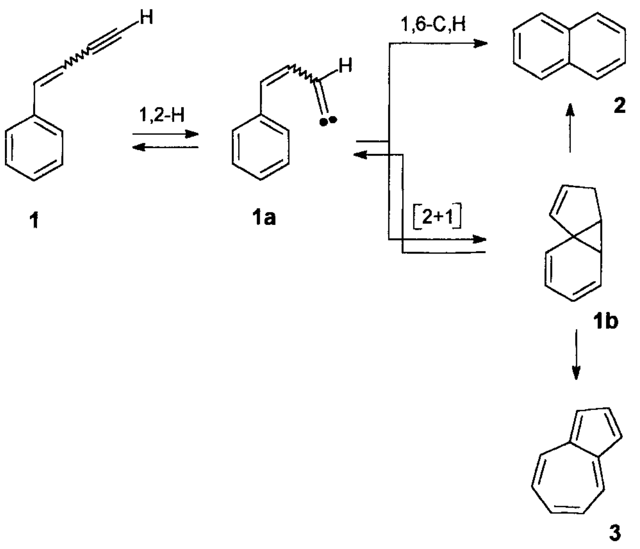
The thermal conversion of 1-phenyl-1-buten-3-yne (**1**) into the cycloisomerization products naphthalene (**2**), azulene (**3**), and 1-methylene-1*H*-indene (**4**) has been studied at temperatures between 550 and 1000°C, a reaction time of approximately 0.3 s at 13 Torr (FVP) and at low partial pressures in a quartz flow system. The results obtained by FVP as well as in the presence of chemically modified diluent gases suggest a predominance of unimolecular cycloisomerizations to **2** and **3** which are, however, always accompanied by radical cyclization reactions to **2** and **4** even under FVP conditions if temperatures above 550°C are applied.

Concurrent with synthetic work on the construction of bowl-shaped[2][3][4] and planar polycyclic aromatics[5][6] as well as compounds with new structures[6] from 1,3-hexadien-5-ynes having partly "masked" C=C double bonds by their integration into aromatic rings, the question of the mechanisms operating at different temperatures are of importance to understand the variety of products which are known to be formed from such hydrocarbons.[1][5][6][7][8]

With respect to the syntheses of corannulene and semibuckminsterfullerene from multiply ethynyl-substituted fluoranthene[2] and 4,5-*o*-phenylenefluoranthene,[4] respectively, the thermal conversion of 1-phenyl-1-buten-3-yne (**1**)[7] is believed to provide a further insight into the corresponding cycloisomerization mechanism, because **1** is formally the simplest hexadienyne having the same structural properties as the precursors mentioned above. Scheme 1 depicts the mechanism which Wentrup et al.[7] have proposed to occur under Flash Vacuum Pyrolysis (FVP, 1000°C, 0.001 Torr) conditions. The alkenylidene carbene species **1a** is thought to control the reaction events, leading to naphthalene (**2**) and azulene (**3**) as the sole isolable cycloisomerization products.

Scheme 1



Very recently published results on the cycloisomerization of 1,4-diphenyl-1-buten-3-yne at temperatures ≥ 600 °C show, however, that at atmospheric pressure and low hydrocarbon concentrations the formation of the corresponding phenylnaphthalenes takes place by three different ring-closure reactions in parallel:[1] a course via alkenylidene carbenes, a second one involving vinyl-type radicals and, thirdly, to a minor extent, one via isoaromatic intermediates formed by electrocyclization (cf. for example ref.[6][8]). Recently published observations on the formation of chain carrier radicals by destructive adsorption of starting hydrocarbons at the hot inner surface of outside heated reactors,[9] suggest that radical reactions may not be excluded a priori even under FVP conditions.

To scrutinize if radical reactions are also able to compete with the reaction course via the alkenylidene carbene species **1a** under FVP conditions in the broadest sense, we repeated the thermal conversion of **1** under FVP conditions but at a vacuum of about 13 Torr and reactor wall temperatures ≤ 1000°C, preferably 550 to 800°C. Furthermore, we carried out these studies under flow-pyrolysis conditions at

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[◇] Part 3: Ref.[1].

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atmospheric pressure in the presence of excess nitrogen and chemically "modifying" diluent gases [$H_2(D_2)$, N_2-toluene and N_2-H_2 mixtures] following the results reported in our earlier publication.[1]

Results

Thermal Conversions of 1-Phenyl-1-buten-3-yne (1)

Flash Vacuum Pyrolysis (FVP): **1** was subjected to FVP as a 10% mixture of 93% *trans*- and 7% *cis*-**1** in benzene and converted at 13 Torr. After passing the tubular quartz reactor (already described in ref.[1]) at reactor wall temperatures between 550 and 1000°C, the effluent was cooled down, collected and analyzed (GC, GC/MS, GC/FT-IR). The main products formed at different reactor wall temperatures are listed in Table 1. It illustrates that at temperatures $\leq$ 800°C 1-methylene-1*H*-indene (**4**) is simultaneously formed as a further significant product in a maximum selectivity (definition see Table 1) of $S = 13$ at 600°C beside **2** and **3**. Minor reaction products also identified are phenylacetylene, styrene, indene, and 2-ethynylstyrene.

Table 1. Dependence of the selectivity S[a] of the reaction products[b] formed by FVP from **1** at reactor wall temperatures between 550 and 1000°C (pressure 13 Torr)

Reactor wall temperature [°C]	550	600	700	800	1000
Conversion [%]	1	10	58	95	98
Products					
2	93	85	90	92	95
3	7	2	2	1	tr.
4	tr.	13	7	4	1

[a] Selectivity S: mol of product formed per 100 mol of **1** converted. – [b] Detected byproducts ($\Sigma S \leq 3$): benzene, phenylacetylene, styrene, indene, and 2-ethynylstyrene.

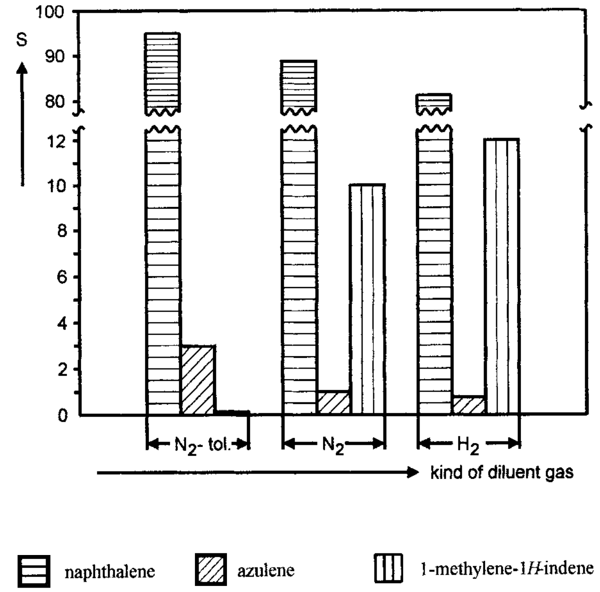
Pyrolysis at Atmospheric Pressure: At temperatures between 550 and 800 °C and a reaction time of approximately 0.3 s, **1** was pyrolyzed in the presence of diluent gases. Thus, a 10% mixtures of **1** in benzene was swept with a stream of a diluent gas (dg) that carried **1** in low concentrations ($n_1/n_{dg} \approx 1{:}50$) through the same tubular quartz reactor as used in FVP. As diluent gases oxygen-free nitrogen (N_2), mixtures of nitrogen-hydrogen (N_2-H_2) and nitrogen-toluene (N_2-tol) containing approximately 5 mol-% of hydrogen and toluene), respectively, pure hydrogen (H_2) and (in some experiments) pure deuterium (D_2) were used in independent runs. After leaving the effective reactor zone, the liquid pyrolyzates (together with the solvent, benzene) were collected and analyzed as above.

The yields of the pyrolyzates amounted to about 95% of the solution of **1** used (quantity used per run: about 0.1 ml). In all experiments, the liquid pyrolyzates consisted of unconverted **1**,[10] naphthalene (**2**), azulene (**3**), 1-methylene-1*H*-indene (**4**), and small amounts of by-products such as phenylacetylene, styrene, indene, and 2-ethynylstyrene (when the pyrolyses were carried out in the presence of N_2 and N_2-tol), but additionally toluene, ethylbenzene, 1- and 3-methylindene, 1,2- and 1,4-dihydronaphthalene, and 1- and 2-phenylnaphthalene (when N_2-H_2 or H_2 was used as diluent gas). Cracked gases $\leq C_4$ were produced in trace amounts only. The amount of benzene, another possible by-product of the decomposition of **1**, could not be determined from these experiments because of its identity with the solvent. Pyrolysis runs carried out independently using fluorobenzene as the solvent instead of benzene, however, show that benzene is formed as a minor product only (maximum yield: 0.5 wt-% at 800 °C in the presence of hydrogen). Table 2 lists the temperature dependence of the product selectivities of **2**, **3**, and **4** formed in the presence of different diluent gases. Figure 1 also informs graphically on the dependence of the product selectivities on the kind of diluent gas employed at 650°C.

Table 2. Dependence of the conversions of **1** and of the selectivities of the formed cycloisomerization products on the diluent gas at different reaction temperatures

Diluent gas	Temperature [°C]	Conversion [%]	Products [S]		
			Naphthalene (**2**)	Azulene (**3**)	1-Methylene-1*H*-indene (**4**)
N_2	550	2	99	1	–
	600	6	96	1	3
	700	42	89	1	9
	800	97	95	1	2
N_2-tol	550	< 1	99	1	–
	600	2	98	2	–
	700	25	95	4	tr.
	800	90	90	5	1
N_2-H_2	550	2	99	1	–
	600	6	87	< 1	12
	700	59	88	< 1	9
	800	98	92	–	1
H_2	550	2	99	1	–
	600	8	85	< 1	14
	700	63	87	< 1	9
	800	99	92	–	1

Figure 1. Dependence of selectivities of the main products from **1** on the kind of diluent gas at 650°C



To gain further information about the role of H atoms during the flow pyrolysis in the presence of hydrogen, several experiments were repeated in the presence of deuterium. At 700 °C and otherwise comparable conditions, the liquid pyrolyzate contained deuterated derivativs of **1** to **4** as essential products. The degree of deuteration was determined by GC-MS analysis, and the results are listed in Table 3.

Table 3. Degree of deuteration of the C_{10} compounds in the pyrolyzate of the conversion of **1** in the presence of deuterium (reaction temperature 700 °C)

Fraction	Deuteration degree[a] [%]
1-phenyl-1-butene-3-yne (**1**)	2.6
naphthalene (**2**)	6.4
azulene (**3**)	2.7
methylene-1*H*-indene (**4**)	12.4

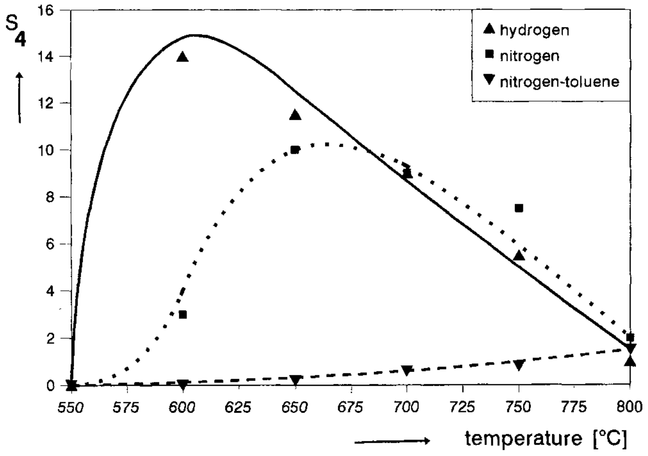
[a] Referred to the corresponding compound ($C_{10}H_8$ equal 100%).

The D incorporation of **3** corresponds within the limits of experimental error to that of the unconverted **1** while the deuteration degree of **2** and particularly **4** was determined to be significantly higher. Moreover, the ^{2}H-NMR spectrum of the liquid pyrolyzate reveals that the D atoms of **2** are preferably located at C-2 [the integral ratio of the D atoms at C-2 (δ = 7.37) and C-1 (δ = 7.77) amounts to about 2.2].

These results show: (a) The products, detected in the pyrolyzates from FVP and atmospheric pressure pyrolysis agree qualitatively. (b) The kind of the diluent gas used clearly influences the composition of the liquid pyrolyzates (Table 2). (c) Under FVP conditions, the selectivity of **3** decreases with increasing temperature while its formation in the presence of diluent gases gains only importance when N_2-tol is used and it is increasingly formed the higher the temperature becomes. (d) **4** could not be detected at pyrolysis temperatures ≥ 550 °C; in the presence of N_2-tol it is detectable in trace amounts only, in the other diluent gases and under FVP conditions, however, its selectivity runs through a maximum (Figure 2).

Thermal Conversion of Azulene (3) and 1-Methylene-1H-indene (4)

Figure 2. Temperature dependence of the selectivity of **4** in the presence of different diluent gases



To check the behavior of the primary cycloisomerization products **3** and **4** were converted as described for **1** at 650, 700 and 750 °C (0.3 s) in the presence of either N_2-tol, N_2, N_2-H_2 or H_2, respectively. Azulene (**3**) was used in the pyrolysis runs as a chemically pure compound, **4** as a 9:1 mixture with indene (see Experimental Section). The results are summarized in Table 4.

Table 4. Dependence of the conversions of **3** and **4** and of the selectivities of **2** on the reaction temperature in presence of different diluent gases

Temperature [°C]	Diluent gas	Substrate			
		3		**4**	
		conv. [%]	S_2[a]	conv. [%]	S_2[a]
650	N_2-tol	0	–	0	–
	N_2	1	100	1	100
	H_2	22	98[b]	18	97[c]
700	N_2-tol	< 1	100	1	100
	N_2	2	100	4	100
	H_2	46	98[b]	33	98[c]
750	N_2-tol	2	100	1	100
	N_2	7	100	7	100
	H_2	74	94[b]	55	97[c]

[a] Selectivity of **2**. – [b] Others ($\Sigma S < 6$): 1,2-dihydronaphthalene, traces of 1,4-dihydronaphthalene. – [c] Others: 1,2-dihydronaphthalene ($S \approx 3$).

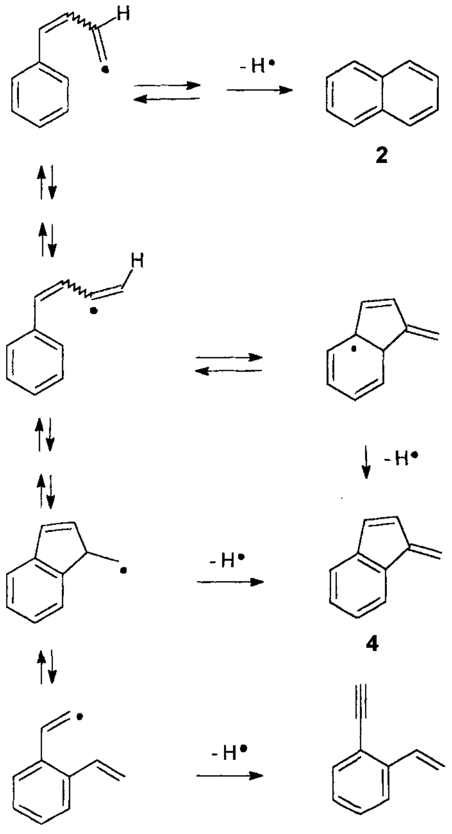
When N_2-tol was used as the diluent gas, the degree of conversion of **3** and **4** amounts to 2% and 1% maximum, respectively, at 750 °C only. The substitution of N_2-tol by N_2 resulted in a marginally higher degree of conversion (7% at 750 °C) and **2** was the only detectable reaction product. When H_2 was used, however, **3** and **4** rearranged significantly faster into **2** than in the presence of other diluent gases. Furthermore small amounts of 1,2-dihydronaphthalene were additionally formed ($S \leq 3$).

Discussion

The results reported above clearly show that the cycloisomerization of **1** is mainly initiated by a 1,2-H shift and terminated by a 1,6-C,H insertion of the reversedly formed alkenylidene carbene **1a** yielding **2**.[7] The participation of electrocyclic[1][6] and radical-controlled ring closures[1][11] during the formation of **2**, however, cannot be excluded, although radical driven cycloisomerizations require a preceding addition of chain carrier radicals (H atoms) to the C–C triple bond of **1**,[1] the probability of which decreases with increasing temperatures because of thermodynamic reasons. But the formation of azulene (**3**) is clearly indicative of the presence of the carbene intermediate **1a** which itself is thought to react not only to **2** but additionally to **3** by intramolecular [2 + 1] cycloaddition. It results first in the three membered ring species **1b** which itself is subjected to C–C bond cleavage that gives **3** in analogy to the interpretation given in ref.[5][7] For an alternate pathway from **1** to **3** there is no precedent. A precise analysis of the pyrolyzate from the FVP experiment of **1** at 1000 °C (13 Torr), however, shows that **2** is nearly the only still detectable cycloisomerization product. As mentioned above experiments at lower reactor wall temperatures show that

1-methylen-1*H*-indene (**4**) is a further reaction product (see Table 1). Its maximum selectivity reached approximately 13 at 600 °C, but with increasing temperature the selectivity decreases. At 550 °C, the degree of conversion of **1** is very small and **4** is formed in trace amounts only. The maximum selectivity as well as the detection of 2-ethynylstyrene can be interpreted by assuming a radical-driven reaction only, as depicted in Scheme 2.

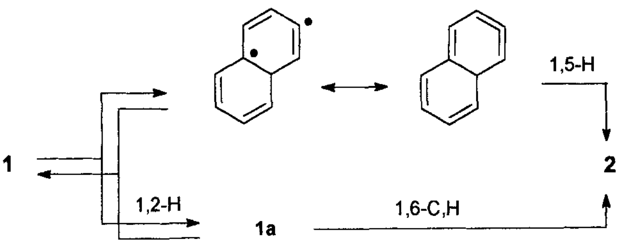
Scheme 2



This process assumes the generation of chain carrier radicals which are known to be formed at temperatures above approximately 600/620 °C.[1][8] The absence of **4** in the pyrolyzate obtained at 550 °C, the formation of decomposition products at temperatures ≥ 600 °C and the decreasing selectivities of **4** as well as of **3** with increasing temperatures above 600 °C agree with the common knowledge of expected radical reactions. This view is impressively confirmed by the results obtained from pyrolysis runs of **1** (Tables 2 and 3), **3** and **4** (Table 4) in the presence of differently reactive diluent gases at atmospheric pressure but low concentrations of the hydrocarbon species. While azulene (**3**) is formed in the presence of the nitrogen-toluene mixture only, the selectivity of **4** is negligible under these conditions. In contrast, the maximum selectivity of **4** oviously increases with growing stationary concentrations of the chain carrier radicals.

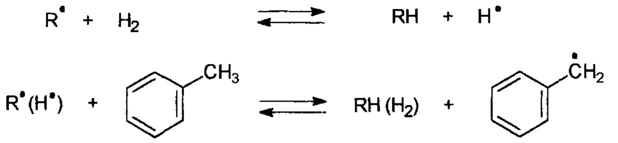
In the presence of nitrogen, the rate of competing uni- (Scheme 3) and bimolecularly initiated (Scheme 2) cycloisomerization reactions depends on the respective temperature only.

Scheme 3



When nitrogen is, however, proportionally or completely substituted by hydrogen, the C-centered chain carrier radicals formed independently by destructive adsorption (see above) are thought to be converted to the greatest possible extent into H atoms (Scheme 4).[12] This gives rise to the highest determined degree of conversion of **1** (Table 2), **3** and **4** (Table 4) at all temperatures, to very low yields of **3** from **1** and also to the fact that the formation of **4** is always passing maxima (Table 2, Figure 2).

Scheme 4



The opposite occurs when nitrogen is proportionally substituted by toluene. This guarantees extensive conversion of reactive chain carrier radicals into less reactive, resonance stabilized benzyl radicals (Scheme 4)[12] which results not only in a certain reduction of the corresponding degrees of conversion, but also in extensive repression of the formation of **4** from **1** and of the radical-controlled rearrangement of **4** into **2** (Table 2). The participation of radical reactions during the thermal conversion of **1** at temperatures ≥ 600 °C is furthermore supported by the incorporation of deuterium atoms into **2**, **3** and **4** and the unconverted **1** as well when **1** is pyrolyzed in the presence of deuterium instead of hydrogen. The degrees of deuteration determined are listed in Table 3. The correspondence of the degrees of deuteration of **3** and **1** support the assumption that the rearrangement of **1** → **3** can hardly be assisted by radicals while the high deuteration degree of **4** indicates the opposite. The degree of deuteration of **2**, however, leads to the conclusion that radical reactions are involved in its formation. This is traced to radical controlled rearrangements of **3** and **4** into **2**, but a direct radical cycloisomerization of **1** to **2** via vinyl-type radicals by analogy to the mechanism described in ref.[1] and depicted in Scheme 2 cannot be ruled out from the experimental results. The determination of the proportions in which the naphthalenes are formed by electrocyclic ring closures and reaction cascades occurring via alkenylidene carbenes and vinyl-type radicals, respectively, from the corresponding 1,3-hexadien-5-ynes is the subject of the following paper.[13]

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Experimental Section

General: GC (total analysis): HP 5890 Series II (25-m column, PS 255, H_2). – GC/MS: HP 5890 Series II (12-m column, SE-54, He)/HP 5971 A. – GC/FT IR: HP 5890 Series II (25-m column, Se 54, N_2)/HP 5965 B. – GC (pyrolysis gases): HP 5890 Series II (50-m column, Al_2O_3/KCl, H_2). – ^{1}H NMR: Varian UNITY 400 (400 MHz; $CDCl_3$ or [D_6]acetone). – ^{2}H NMR: Varian UNITY 400 (61 MHz, acetone). – ^{13}C NMR: Varian UNITY 400 (100 MHz; $CDCl_3$ or [D_6]acetone).

Low Partial Pressure Pyrolysis at 760 Torr: The pyrolyses were carried out in the presence of oxygen-free diluent gases [nitrogen, hydrogen (deuterium), molar mixtures of nitrogen-toluene or nitrogen-hydrogen (ca. 20:1, in each case)] using a tubular flow reactor as described previously (quartz, D_i: 10 mm, l: 300 mm, electrically heated).[1] The amount of carrier gas used was controlled by flow meters in each case. The starting compounds were introduced as 10% mixtures with benzene (or fluorobenzene) by a 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 substrate mixture to the temperature guaranteeing a loading of the gas stream with 2% of the substrate mixture. The reaction temperature was varied between 550 and 800 °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 separated from the diluent and some cracked gases. All products were analyzed and identified by GC, GC/MS and GC/FT-IR analysis. The gas analyses were carried out by means of closable sampling columns.[14]

Flash Vacuum Pyrolysis (FVP): For the FVP experiments, an electrically heated quartz reactor (D_i: 10 mm, l: 300 mm, unpacked) was used operating at 13 Torr. The substrate mixture was introduced through a glass column (D_i: 0.05 mm, l: 200 mm) into a thermostated vaporizer filled with quartz wool as described above. After leaving the reactor, the product mixture was rapidly cooled down (liquid nitrogen) and collected. The products were analyzed and identified as above.

1-Phenyl-1-buten-3-yne (**1**): 9.2 g (0.05 mol) of 1-phenyl-2-bromoethene was treated according to ref.[15] with 5.9 g (0.06 mol) of trimethylsilylacetylene in 100 ml of piperidine. After addition of 0.18 g of palladium(II) chloride, 0.30 g of triphenylphosphane and 0.05 g of copper(I) iodide, the mixture was stirred for 4 h at room temperature. The piperidine was removed by distillation (50 Torr) and the residual product extracted three times with benzene. The benzene phase was treated with dilute hydrochloric acid, washed with water, dried with sodium sulfate, the solvent removed by distillation, and the residual trimethylsilyl-protected compound was purified by column chromatography with hexane on Al_2O_3 (type 507 C, 100–125 mesh) yielding a *cis*/*trans* (7:93) mixture of 1-phenyl-4-(trimethylsilyl)-1-buten-3-yne (**5**) (yield 58%). – *trans*-**5**: MS; *m*/*z* (%): 200 (39) [M^+], 186 (18), 185 (100), 169 (14), 155 (9), 141 (7), 129 (7), 115 (8), 43 (14). – IR (FT IR): $\tilde{\nu}$ = 3084 cm^{-1}, 3037, 2966, 2907, 2119, 1954, 1783, 1262, 1078, 951, 880. – *cis*-**5**: MS; *m*/*z* (%): 200 (39) [M^+], 186 (18), 185 (100), 169 (14), 155 (9), 141 (7), 129 (7), 115 (8), 43 (14). – IR (FT IR): $\tilde{\nu}$ = 3084 cm^{-1}, 3037, 2966, 2907, 2139, 1946, 1494, 1403, 1261, 1017, 854, 773. – 4 g (0.02 mol) of 1-phenyl-4-(trimethylsilyl)-1-buten-3-yne (**5**) was dissolved in methanol (50 ml), 25 ml of a 1 N aqueous solution of potassium hydroxide added, and the mixture stirred for 3 h at room temperature. After addition of ether (100 ml), the organic layer was separated, washed with water, dried with magnesium sulfate, and the crude **1** purified by column chromatography with hexane (adsorbent: LiChroprep Si 100) to give a *cis*/*trans* (7:93) mixture of 1-phenyl-1-buten-3-yne (**1**) (yield 58%). – *trans*-**1**: MS; *m*/*z* (%): 128 (100) [M^+], 127 (25), 126 (10), 102 (18), 78 (6), 63 (5), 51 (6). – IR (FT IR): $\tilde{\nu}$ = 3329 cm^{-1}, 3074, 3044, 2108, 1799, 1597, 1498, 1455, 952. – ^{1}H NMR ([D_6]acetone): δ = 7.1 (d, 1-H), 6.4 (dd, 2-H), 3.5 (d, 4-H), 7.38–7.44 (m, aromatic H). – *cis*-**1**: MS; *m*/*z* (%): 128 (100) [M^+], 127 (24), 126 (9), 102 (18), 78 (6), 63 (5), 51 (6). – IR (FT IR): $\tilde{\nu}$ = 3323 cm^{-1}, 3068, 3044, 2091, 1946, 1884, 1739, 1680, 1601, 1494, 1400, 1222, 948, 783.

Azulene (**3**) (commercial product from FLUKA) was recrystallized from hexane before use in the pyrolysis experiments.

1-Methylene-1H-indene (**4**) was prepared from indene and gaseous formaldehyde as described in ref.[16] (see also ref.[1]). Recrystallization of the crude product from *n*-hexane gave a 9:1 mixture of **4** and indene (yield 20%) which was directly used for the pyrolysis runs. – ^{1}H NMR ([D_6]acetone): δ = 5.75 (s), 6.15 (s) 6.54 (d), 6.90 (d), 7.65 (d), 7.1–7.3 (m). – ^{13}C NMR ([D_6]acetone): δ = 115.1 (t), 121.0 (d), 122.0 (d), 126.5 (d), 129.2 (d), 131.0 (d), 134.4 (d), 144.8 (s), 144.9 (s), 149.1 (s).

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[10] Under the conditions of our experiments, *trans*-**1** is, of course, partly converted into *cis*-**1**. At 550 °C the *trans*/*cis* ratio was determind to be about 2.7. Above 600 °C, the ratio amounts to about 1.8, it is independent of the kind of diluent gas used in each case.

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