Flash vacuum thermolysis of 5-(1-chloroethenyl)acenaphthene. A short synthesis of pyracylene and its behaviour under high temperature conditions†

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Flash vacuum thermolysis (FVT) of 5-(1-chloroethenyl)acenaphthene (4) has been found to give rise to pyracylene (1). Pure 1 can be isolated from the 1100 °C pyrolysate by recrystallization at − 20 °C. The temperature conversion data reveal that 1 decomposes and rearranges at $T \geqslant 1000$ °C; acenaphthylene (11), 1-ethynyl- (23) and 3-ethynyl-acenaphthylene (24) have been identified. The formation of 23 and 24 indicates that 1 rearranges to the transient cyclopent[*bc*]acenaphthylene (20) *via* a single ring-contraction–ring-expansion mechanism under FVT conditions. The experimental data are supported by semiempirical AM1 calculations of the $C_{14}H_8$ potential energy surface.

Introduction

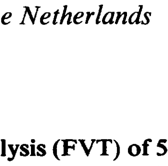
Although it has recently been shown that pyracylene (cyclopent[*fg*]acenaphthylene $C_{14}H_8$, 1), despite its formal 12π electron perimeter, is a stable hydrocarbon, its chemistry is still unexplored as a consequence of the difficulties encountered in its synthesis.[1,2] This is unfortunate since 1 possesses interesting electronic properties for the application in material science, *i.e.* for ladder-type π-conjugated polymers[3] and (semi)-conducting organic metal salts.[4] In addition, 1 is a fullerene key-substructure and draws attention as a reference compound to rationalize their chemistry.[5] Furthermore, 1 has been proposed to be one of the most stable $C_{14}H_8$ polycyclic aromatic hydrocarbons (PAH) under high temperature conditions on the basis of thermodynamic considerations.[6]


1


4


8


11


23


24

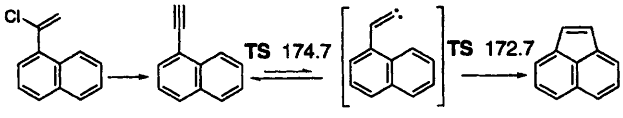
At the moment the best preparations of 1 involve flash vacuum thermolysis (FVT) of precursors such as pyrene-1,6- and pyrene-1,8-dione,[2,7] 1,3,5,8-tetrachloromethylnaphthalene[8] and 1,5-diethynylnaphthalene.[9] However in all cases, laborious purification procedures are required to isolate pure 1 in low yield.

Here we report a short FVT synthesis of pyracylene (1) from the readily accessible precursor 5-(1-chloroethenyl)acenaphthene (4); pure 1 can be isolated from the 1100 °C pyrolysate by a simple recrystallization procedure. Moreover, analysis of the pyrolysate product composition at $T \geqslant 1000$ °C provides an insight into the high temperature behaviour of 1. It is shown that, besides the major products 5-ethynylacenaphthylene (8) and 1, three side-products, acenaphthylene (11), 1-ethynyl- (23) and 3-ethynyl-acenaphthylene (24), are present. These observations are of relevance with respect to the proposal that 1 is a prevalent effluent during combustion of hydrocarbon-containing fuels and in flame processes[10] and with regard to the propensity of 1 to undergo rearrangements[11] under high temperature conditions (*vide infra*).

Results and discussion

Based on the following experimental and theoretical considerations 5-(1-chloroethenyl)acenaphthene (4) was identified as a novel FVT precursor for pyracylene (1).

In previous work we have shown that 1-(1-chloroethenyl)-naphthalene (14) is an excellent FVT precursor for 1-ethynylnaphthalene (13), which under high temperature conditions (10^{-2} Torr, 1000 °C, unfilled quartz tube) is quantitatively converted into acenaphthylene (11, yield 80%). The formation of 11, *i.e.* the occurrence of cyclopenta-fusion, was rationalized by invoking an ethynyl (13)–ethylidene carbene (12) rearrangement followed by an intramolecular carbene insertion into an aromatic C–H bond (Scheme 1).[12]



14 13 96.1 12 156.8 11 80.7

Scheme 1

FVT (10^{-2} Torr, evaporation temperature 120 °C and evaporation rate 0.3 g h^{-1}, see Experimental section) of the bis-functionalized analogue of 14, *i.e.* 1,5-bis(1-chloroethenyl)naphthalene (15), between 700 °C $\leqslant T \leqslant$ 900 °C gave 1,5-diethynylnaphthalene (16),[9] which is an FVT precursor of 1. Indeed at $T \geqslant 700$ °C, 16 is converted to 5-ethynylacenaphthylene (8) and at $T \geqslant 900$ °C pyracylene (1) is identified. However, under the conditions required for complete conversion of 14 to 11 (T 1000 °C, *vide supra*), compound 15 does not give 1 in

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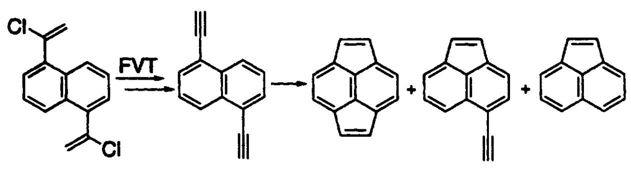
† Part of this work has been presented at the 8th International Symposium on Novel Aromatic Coumpounds, 1995, Braunschweig, Germany, July 30–August 4; L. W. Jenneskens, lecture 7.

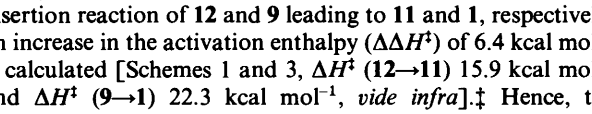
quantitative yield. Instead of **1**, compound **8** is still the major product (Scheme 2, Table 1 and Experimental section).



15 **16** **1** **8** **11**

Scheme 2

Although at $T \geqslant 900$ °C the yield of **8** decreases from 78% to *ca.* 55%, a concomitant decrease in the yield of **1** from 33% to 22% in going from 1000 to 1100 °C was found at the expense of mainly one novel product acenaphthylene (**11**; 1000 °C, yield 9% and 1100 °C, yield 24%). In addition, at 1100 °C, two other products 1-ethynyl- (**23**;[13] 1100 °C, trace amount) and 3-ethynyl-acenaphthylene (**24**;[13] 1100 °C, yield 2%), were unequivocally identified. These results suggest that **1**, in contrast to **11**, both decomposes and rearranges at $T \geqslant 1000$ °C (*vide infra*). A rationalization for these observations is provided by semiempirical AM1[14] calculations (Schemes 1–3, *vide infra*).‡ For both the ethynyl–ethylidene carbene rearrangement as well as the intramolecular carbene C–H insertion reaction minima and transition states were located using the appropriate routines as implemented in MOPAC 6.0 (see Experimental section). Note that AM1 tends to overestimate activation enthalpies ($\Delta H^{\ddagger}$) values for 1,2-H shifts[14] such as is operational for the ethynyl–ethylidene carbene rearrangement. The conversion of **8** ($\Delta_f H^\circ$ 135.8 kcal mol^{-1}) to **1** ($\Delta_f H^\circ$ 135.6 kcal mol^{-1}) is predicted to be 15.2 kcal mol^{-1} [$\Delta\Delta_f H^\circ$ (**8**→**1**) -0.2 kcal mol^{-1}] less exothermic than that of **13** ($\Delta_f H^\circ$ 96.1 kcal mol^{-1}) to **11** [$\Delta_f H^\circ$ 80.7 kcal mol^{-1} with $\Delta\Delta_f H^\circ$ (**13**→**11**) -15.4 kcal mol^{-1}]. The value of $\Delta\Delta_f H^\circ$ (**8**→**1**) -0.2 kcal mol^{-1} indicates that compounds **8** and **1** will equilibrate under high temperature conditions. The decrease in $\Delta\Delta_f H^\circ$ for the conversion of **8** to **1** compared with that of **13** to **11** can be rationalized by the increase in strain energy ($E_S = -\Delta_r H$) due to the second cyclopenta-fusion. The AM1 E_S of **1**, *i.e.* 14.8 kcal mol^{-1},[1] calculated using the following homodesmotic equation [reaction (1)] is in excellent



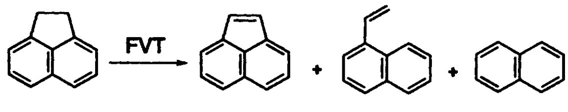
(1)

1 **11**

135.6 40.6 2 x 80.7

agreement with previously reported *ab initio* estimates (E_S; RHF/6-31G* 15.1 kcal mol^{-1} and RMP2/6-31G* 14.7 kcal mol^{-1}).[15] Furthermore, for the intramolecular carbene C–H insertion reaction of **12** and **9** leading to **11** and **1**, respectively, an increase in the activation enthalpy ($\Delta\Delta H^{\ddagger}$) of 6.4 kcal mol^{-1} is calculated [Schemes 1 and 3, $\Delta H^{\ddagger}$ (**12**→**11**) 15.9 kcal mol^{-1} and $\Delta H^{\ddagger}$ (**9**→**1**) 22.3 kcal mol^{-1}, *vide infra*].‡ Hence, the calculations indicate that the conversion of **15** to **1** will become more difficult due to thermodynamic and kinetic factors.

Another way to introduce a fused cyclopentene moiety under high temperature conditions is *via* hydrogen abstraction from an already fused cyclopentane unit. To gain insight into this process the high temperature FVT behaviour of acenaphthene (**2**) was investigated (FVT, 10^{-2} Torr, evaporation temperature 120 °C and evaporation rate 0.3 g h^{-1}, see Experimental section). The temperature conversion data show that acenaphthylene (**11**) is the primary product [reaction (2), Table 2 and Experimental section]. The results suggest that in the temperature range 700 °C $\leqslant T \leqslant$ 1100 °C hydrogen abstraction occurs less readily than intramolecular carbene insertion in the case of **12** (Scheme 1, and Tables 2 and 3). Notwithstanding, at $T \geqslant 1000$ °C fragmentation processes become competitive; both 1-ethenylnaphthalene (**17**) and naphthalene (**18**) were unequivocally identified as side products in the pyrolysates (Table 2).



(2)

2 **11** **17** **18**

Table 1 Product composition of the pyrolysates obtained from FVT of **15**[a]

		Product composition (%)						
T/°C	Recovery (%)	**15**	**16**	**8**	**1**	**11**	**23**	**24**
700	93	7	73	20	—	—	—	—
800	93	6	58	35	1	—	—	—
900	70	1	19	78	2	—	—	—
1000	68	—	—	58	33	9	—	—
1100	57	—	—	52	22	24	*b*	2

[a] ^{1}H NMR integral ratios, capillary GC and HPLC data are in agreement. [b] Trace amount.

Taking into account these considerations we envisaged that upon FVT of 5-(1-chloroethenyl)acenaphthene (**4**) the undesired formation of 5-ethynylacenaphthylene (**8**) can be suppressed to some extent.

FVT of 5-(1-chloroethenyl)acenaphthene (4). Compound **4** was prepared from acenaphthene (**2**) in two steps. Conversion of **2** into 5-acetylacenaphthene (**3**, yield 86%) followed by treatment with PCl_5 gave 5-(1-chloroethenyl)acenaphthene (**4**) in 72% yield after purification (Scheme 3 and Experimental section).

Aliquots of **4** (0.1 g) were slowly evaporated into the unpacked quartz tube of our FVT apparatus at the temperatures shown in Table 3 (10^{-2} Torr, evaporation temperature 85 °C and evaporation rate 0.3 g h^{-1}, Experimental section). Analysis of the pyrolysates (^{1}H, ^{13}C NMR, GC, GC–MS and HPLC) showed that in the temperature range 700–900 °C compound **4** is converted into 5-ethynylacenaphthene (**5**) and, subsequently, into both 1,2-dihydropyracylene (**7**)[1] and 5-ethynylacenaphthylene (**8**). Since **7** is already present in the 800–900 °C pyrolysates, formation of the second cyclopentene moiety occurs more readily in the case of **5** (*vide supra*). The temperature conversion data show that in the temperature range 900–1100 °C **7** and, to a minor extent **8**, are further converted into **1**, which deposits as deep red crystals behind the hot zone of the furnace. Note that up to 1000 °C, mass recoveries remain good to excellent (Table 3). Concurrent with the decrease in mass recovery at $T \geqslant 1000$ °C a thin carbon lining inside the quartz tube is formed. In line with the results found for 1,5-bis(1-chloroethenyl)naphthalene (**15**) 1-ethynyl- (**23**)[13] and 3-ethynyl-acenaphthylene (**24**)[13] were unambiguously identified as side-products. Furthermore, fragmentation reactions become competitive at $T \geqslant 900$ °C, 5-ethenylacenaphthylene (**10**) and acenaphthylene (**11**), presumably derived from **7** and **1**, respectively, are found. Similar

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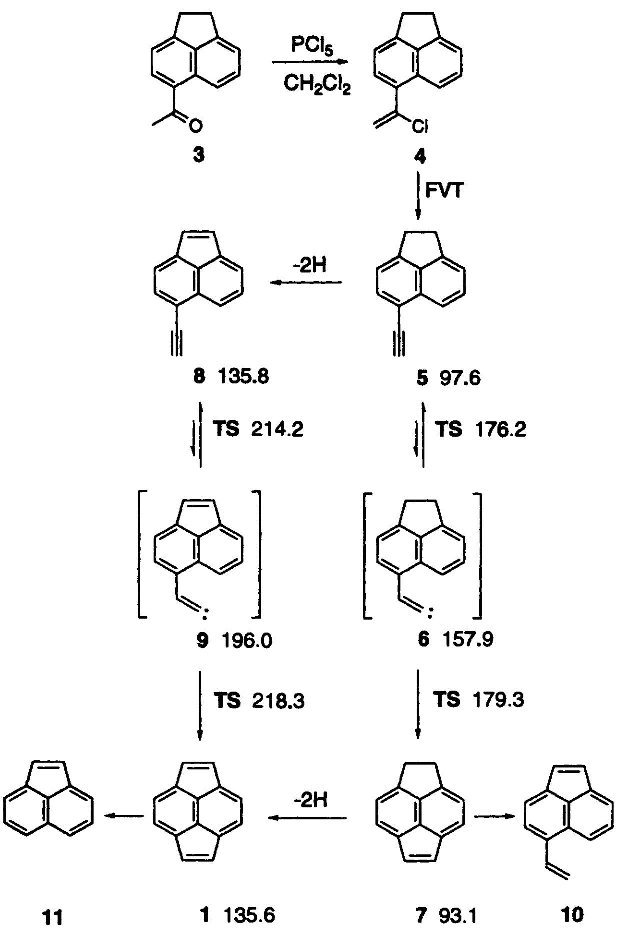
‡ 1 kcal mol^{-1} = 4.184 kJ mol^{-1}. Since the structural features of the AM1[14] optimized geometries of all calculated minima and transition states (TS) are within expectation, we refrain from an extensive discussion. Data concerning the geometry optimization, optimized geometries and the Hessian calculations are available upon request from one of the authors (L. W. J.).



Scheme 3

Table 2 Product composition of the pyrolysates obtained from FVT of **2**[a]

		Product composition (%)			
T/°C	Recovery (%)	**2**	**11**	**17**	**18**
700	99	99	1	—	—
800	98	93	7	—	—
900	94	50	47	2	1
1000	85	13	83	1	3
1100	54	—	93	—	7

[a] ^{1}H NMR integral ratios, capillary GC and HPLC data are in agreement.

behaviour was found for cyclopenta[*cd*]fluoranthene, *i.e.* the benz[a]-fused analogue of **1**.[16]

Although **1** is the major product at 1000 °C (yield 61%), its purification is impaired by the presence of a small amount of 1,2-dihydropyracylene (**7**, yield 3%), which co-deposits behind the hot zone; **1** can only be isolated using preparative column chromatography. Analytically pure pyracylene (**1**) can be readily isolated from the 1100 °C pyrolysate using a simple recrystallization procedure (see Experimental section). The availability of **4** in combination with the simple purification of **1** from the 1100 °C pyrolysate enables routine preparations of 0.2 g quantities in a single FVT run (required starting material **4**, 1.90 g, 8.8 mmol).

Pyracylene (1): a prevalent combustion effluent? The temperature conversion data reported in Tables 1 and 3 also shed light on the still unresolved question as to whether pyracylene (**1**) will be one of the (prevalent) cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAH) in soots obtained from incomplete combustion of hydrocarbon fuels such as ethene, ethyne, liquid fossil fuels, wood and coal.[10,17] Our FVT results obtained for **4** as well as **15** show that **1** already decomposes at $T \geqslant 1000$ °C giving mainly acenaphthylene (**11**, Tables 1 and 3).

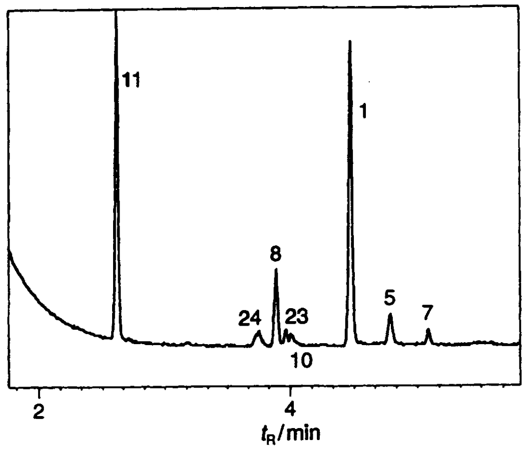


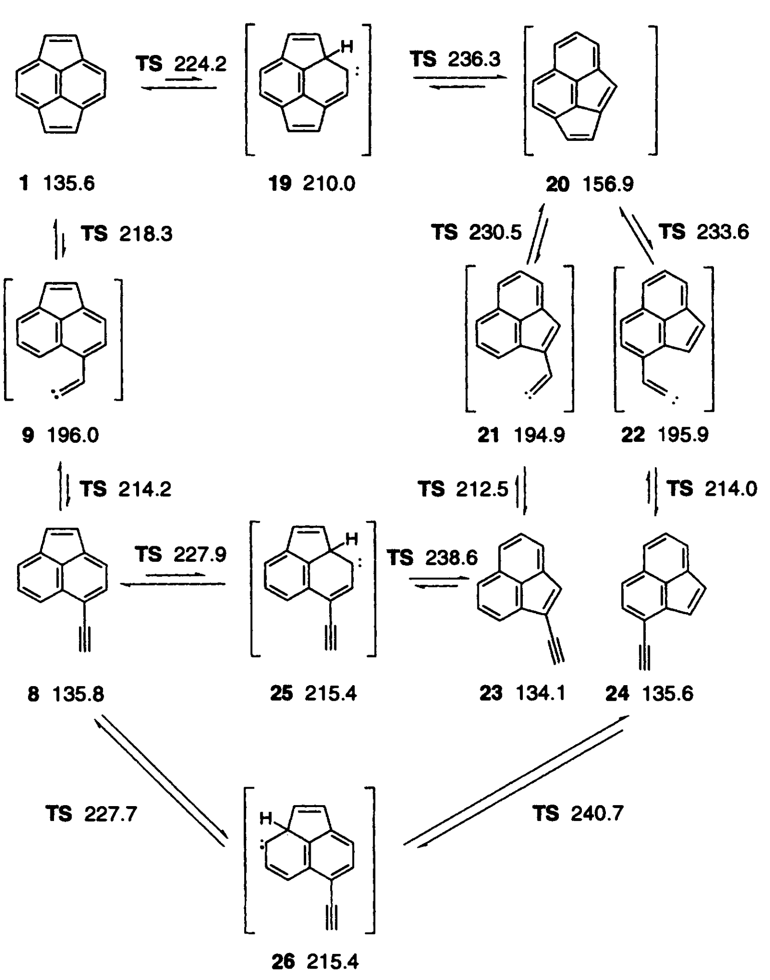
Fig. 1 GC trace of the 1100 °C pyrolysate obtained by FVT of **4** (see Schemes 3 and 4). [Similar chromatograms were also obtained with HPLC (see Experimental section).]

Table 3 Product composition of the pyrolysates obtained from FVT of **4**[a]

		Product composition (%)								
T/°C	Recovery (%)	**1**	**4**	**5**	**7**	**8**	**10**	**11**	**23**	**24**
700	97	—	18	81	1	—	—	—	—	—
800	97	1	15	73	10	1	—	—	—	—
900	84	7	13	38	19	14	8	1	—	—
1000	64	60	—	—	3	18	6	11	1	1
1100	42	44	—	—	—	18	*b*	31	4	3

[a] ^{1}H NMR integral ratios, capillary GC and HPLC data are in agreement. [b] Trace amount; only discernible with capillary GC (see Fig. 1).

Previously one of two overlapping peaks in the gas chromatogram of an extractable soot fraction both with mass m/z 176 ($C_{14}H_8$) has been assigned to **1**.[17] However, it has subsequently been shown that **1** possesses a different retention time under similar analytical conditions.[2] GC–MS and HPLC analyses of the pyrolysates obtained from either **4** or **15** in the temperature range 800–1100 °C unequivocally show that both 5-ethynylacenaphthylene (**8**) and its 1-ethynyl (**23**) and 3-ethynyl (**24**) isomers possess retention times close to that of **1**. As an illustration the capillary gas chromatogram of the pyrolysate obtained by FVT of **4** at 1100 °C is presented in Fig. 1. In addition it should be pointed out that pyracylene (**1**), in line with other (CP)-PAHs such as acenaphthylene (**11**) and biphenylene,[18] possesses a markedly different behaviour under high temperature conditions in either the (dilute) gas phase or the condensed state. Although **1** can be conveniently prepared under FVT conditions, repyrolysis is thwarted due to the fact that **1** cannot be sublimed (temperature range 85–130 °C) from the sample bulb into the hot zone! During heating either under vacuum (10^{-2} Torr) or under an inert atmosphere (N_2) the characteristic deep-red colour of **1** gradually disappears (solid-state UV–VIS–NIR spectroscopy) at the expense of the formation of an intractable colourless material. Extraction experiments of the heat-treated material revealed that no low molecular weight compounds are present. These results indicate that carbon network formation takes place in the condensed state. Additional evidence for the occurrence of a solid-state reaction was obtained by differential scanning calorimetry (DSC) and thermogravimetry (TGA). Whereas in the DSC curve of **1** only one exotherm (ΔH 14.8 kcal mol^{-1}, onset 130 °C) was found, TGA revealed that during this process no



Scheme 4

weight loss occurs. FTIR spectroscopy of the intractable solid formed during heat treatment showed that concomitant with the colour change from deep-red to colourless a new ν_{C-H} stretch vibration positioned at 2900 cm^{-1} becomes discernible. This suggests that the cyclopentene-type double bonds are prone to oligo- cq. polymerization. Similar observations have been reported previously for the $C_{20}H_{10}$ CP–PAHs cyclopent[*fg*]-, cyclopent[*jk*]- and cyclopent[*mn*]-acepyrylene.[19] Thus, the peak with mass *m*/*z* 176 in the gas chromatogram of an extractable soot fraction assigned previously to **1** presumably has to be reassigned to one of the ethynyl substituted acenaphthylene derivatives **8**, **23** and **24**. Note that the formation of ethynyl-substituted PAH under flame conditions is well established.[20]

Rearrangements of pyracylene (1) under high temperature FVT conditions. The high temperature behaviour of pyracylene (**1**) is also of interest with respect to the Stone–Wales rearrangement[11] put forward to rationalize fullerene isomerization *via* the mutual exchange of two five- and two six-membered rings.[11] In the case of **1** this is a degenerate process which can only be detected using selective ^{13}C labelling.§ Close scrutiny of the $T \geqslant 1000$ °C pyrolysates obtained from **4** [and also **15** (Table 1)] revealed that, besides **11**, two novel products identified as 1-ethynyl- (**23**, *T* 1000 °C, 1% and *T* 1100 °C, 4%) and 3-ethynyl-acenaphthylene (**24**, *T* 1000 °C, 1% and *T* 1100 °C 3%) were present (Table 3 and Scheme 4). Their formation can be rationalized by invoking a single five- and six-membered ring shift *via* a ring-contraction–ring-expansion mechanism involving a consecutive 1,2-H (**1**→**19**) and 1,2-C shift (**19**→**20**) or *vice versa*. In the case of **1**, this would give cyclopent[*bc*]acenaphthylene (**20**), which has been proposed previously as a transient intermediate for the interconversion of **23** to **24** and *vice versa* under high temperature FVT conditions.[13] The viability of this process is supported by pyrolysis of independently synthesized 1-ethynylacenaphthylene (**23**) at 1100 °C. The pyrolysate consisted of starting material **23** (49%), its isomers **24** (13%), **8** (3%) and pyracylene (**1**, 3%), acenaphthylene (**11**, 31%) and a trace of phenanthrene (1%).¶ Notwithstanding, it should be noted that **23** as well as **24** can also be obtained directly from 5-ethynylacenaphthylene (**8**) *via* a ring-contraction–ring-expansion mechanism involving a consecutive 1,2-H and 1,2-C shift or *vice versa* in their acenaphthylene moieties, *i.e.* *via* carbenes **25** and **26**, respectively (Scheme 4). In the case of acenaphthylene (**11**) compelling evidence for the occurrence of this process has been obtained using selective ^{13}C labelling.[21] However, AM1 calculations suggest that the $\Delta H^{\ddagger}$ values for the conversion of **23** and **24** into **25** and **26**, respectively [1,2-C shift, $\Delta H^{\ddagger}$ (**23**→**25**) 104.5 kcal mol^{-1} and $\Delta H^{\ddagger}$ (**24**→**26**) 105.1 kcal mol^{-1}] is *ca.* 26 kcal mol^{-1} less favourable than the $\Delta H^{\ddagger}$ values for the conversion of **23** and **24** into the ethylidene carbenes **21** and **23**, respectively [1,2-H shift, $\Delta H^{\ddagger}$ (**23**→**21**) 78.4 kcal mol^{-1} and $\Delta H^{\ddagger}$ (**24**→**22**) 78.4 kcal mol^{-1}].‖ Taking into account that AM1

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§ According to the Woodward and Hoffman rules the Stone–Wales rearrangement[11] is thermally forbidden. A high activation barrier ($\Delta H^{\ddagger}$) is predicted both by semiempirical and *ab initio* calculations.[29]

¶ Similar results have been obtained independently by Necula and Scott, see ref. 30.

‖ For the 1,2-C shift of acenaphthylene (**11**, $\Delta_f H^{\circ}$ 80.7 kcal mol^{-1}) a $\Delta H^{\ddagger}$ 104.8 kcal mol^{-1} was calculated using AM1.[31]

overestimates $\Delta H^{\ddagger}$ for 1,2-H shifts,[14] the latter process is predicted to be considerably more favourable. The AM1 results indicate that the conversion of **23** (**24**) to **20** *via* **21** (**22**) is preferred over the conversion of **23** (**24**) to **8** *via* **25** [(**26**), Scheme 4]. Hence, the formation of **23** and **24** upon FVT of **15** and **4**, respectively, is best rationalized by invoking the rearrangement of **1** to **20** *via* **19** under high temperature FVT conditions.

Conclusions

FVT of 5-(1-chloroethenyl)acenaphthene (**4**) gives convenient access to pyracylene (**1**) which can be isolated *via* a simple recystallization procedure. The temperature conversion data reveal that, despite the prediction that **1** is one of the most stable $C_{14}H_8$ isomers,[6] at $T \geqslant 1000$ °C, **1** decomposes to acenaphthylene (**11**). In contrast to previous contentions, the results strongly suggest that due to its thermal instability **1** will not be a prevalent combustion effluent. Analysis of the 1000–1100 °C pyrolysates unambiguously revealed the formation of the $C_{14}H_8$ isomers 1-ethynyl- (**23**) and 3-ethynyl-acenaphthylene (**24**) providing evidence for the occurrence of a hitherto unobserved rearrangement of **1** *via* the transient intermediate cyclopent[*bc*]acenaphthylene (**20**)[13] under high temperature FVT conditions.

Experimental

General

All reactions were carried out under a N_2 atmosphere. All solvents were purified and dried by standard procedures. Column chromatography was performed on Merck Kieselgel 60 silica (230–400 ASTM). Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 300 spectrometer. *J* values are given in Hz. IR spectra were recorded with an FTIR Mattson Galaxy FTIR 5000 using a diffuse reflection accessory; samples were diluted in optically pure potassium bromide. For solid-state UV–VIS–NIR spectroscopy a CARY 5 spectrophotometer equipped with a praying mantis diffuse reflection accessory was used; samples were diluted in optically pure potassium bromide. GC–MS spectra were collected on a ATI Unicam Automass System 2 quadrupole mass spectrometer (column: J&W Scientific DB-17, length 30 m, id 0.32 mm and film thickness 0.25 μm; injector temperature, 300 °C; temperature program, 2 min, 200→280 °C (10 °C min^{-1}); carrier gas He). HPLC: column reverse phase C_{18} (3 μm particles, diameter 4.6 mm and length 10 cm), Thermo Separation Products Spectra Series 200 gradient pump, Spectra-Physics UV2000 UV detector (λ 254 nm) and eluent acetonitrile–water 60:40. Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 12E under an N_2 atmosphere (heating and cooling rate of 5 °C min^{-1}) and thermogravimetry [TGA(N_2 atmosphere)] was done on a Perkin-Elmer TGS-2 equipped with an autobalance AR-2 (heating rate 20 °C min^{-1}).

5-Acetylacenaphthene (3).[22] To a cooled suspension (0 °C, ice bath) of anhydrous $AlCl_3$ (21.34 g, 160 mmol) in CH_2Cl_2 (150 ml), 12.17 g (155 mmol) acetylchloride was added under stirring. Subsequently, 23.13 g (150 mmol) of acenaphthene (**2**) was added in small portions at room temperature. After heating at reflux temperature for 3 h the reaction mixture was cooled (0 °C, ice bath) and a 1 M HCl solution (100 ml) was added. The organic layer was separated, washed with a saturated sodium bicarbonate solution (100 ml) and water (100 ml), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Crude 5-acetylacenaphthene (**3**, 25.3 g, 129 mmol, 86%) containing 2% of the 3-acetyl isomer was obtained. Although crude **3** can be directly used in the chlorination reaction, it can be purified according to the following procedure. After dissolving crude **3** (129 mmol) in boiling C_2H_5OH (200 ml), picric acid (30 g, 131 mmol) is added. Upon cooling to room temperature orange crystals (picrate charge-transfer complex of **3**) precipitate, which are filtered off and recrystallized from C_2H_5OH (1.25 g ml^{-1}). To obtain pure **3** its picrate salt is dissolved in CH_2Cl_2 (250 ml) and washed with NH_4OH (3 × 75 ml). After concentration of the organic phase under reduced pressure **3** is obtained as a white solid. Yield 19.1 g (97.5 mmol, 65%, mp 68–69 °C). δ_H(300 MHz, $CDCl_3$) 8.74 (1 H, d, *J* 8.6, Ar), 8.07 (1 H, d, *J* 7.3, Ar), 7.60 (1 H, dd, *J* 8.6 and 6.9, Ar), 7.37 (1 H, d, *J* 6.9, Ar), 7.30 (1 H, d, *J* 7.3, Ar), 3.39 (4 H, m, cyclopentane unit) and 2.73 (3 H, s, $COCH_3$); δ_C(75 MHz, $CDCl_3$) 220.2, 153.1, 146.0, 139.7, 132.9, 130.4, 130.1, 129.3, 122.5, 120.4, 118.1, 30.5, 30.3 and 29.0; *m*/*z* (MS) 196 ($M^{\cdot +}$).

5-(1-Chloroethenyl)acenaphthene (4). To a cooled solution (0 °C, ice bath) of **3** (4.35 g, 22.2 mmol) in CH_2Cl_2 (200 ml), PCl_5 (6.16 g, 29.6 mmol) was added. After stirring for 5 h at 0 °C, water (200 ml) was added. The organic layer was separated, washed with a saturated sodium bicarbonate solution (150 ml) and water (150 ml), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Crude 5-(1-chloroethenyl)naphthalene (**4**) was purified by column chromatography (silica, eluent CH_2Cl_2). Yield **4**, 3.44 g (16 mmol, 72%, brownish oil). δ_H(300 MHz, $CDCl_3$) 7.97 (1 H, d, *J* 8.3, Ar), 7.58 (1 H, d, *J* 7.1, Ar), 7.54 (1 H, dd, *J* 8.3 and 7.2, Ar), 7.35 (1 H, d, *J* 7.1, Ar), 7.28 (1 H, d, *J* 7.2, Ar), 5.84 (1 H, d, ^2J 1.1, ArCClCH*H*), 5.64 (1 H, d, ^2J 1.1, ArCClC*H*H) and 3.41 (4 H, m, cyclopentane unit); δ_C(75 MHz, $CDCl_3$) 147.9, 146.3, 139.4, 138.5, 132.1, 128.8, 128.6, 128.5, 120.6, 119.7, 118.6, 116.7, 30.5 and 30.2; *m*/*z* (MS) 214 ($M^{\cdot +}$ with isotope pattern).

1,5-Bis(1-chloroethenyl)naphthalene (15).[23] 1,5-Bis(acetyl)-naphthalene[24] (0.24 g, 1.1 mmol) was treated with PCl_5 (0.54 g, 2.6 mmol) in CH_2Cl_2 (17 ml) at reflux temperature for 4.5 h. After cooling to room temperature, water (25 ml) was added to the reaction mixture. After work-up (see compound **4** for procedures) crude **15** was purified by column chromatography (silica, eluent $CHCl_3$–C_6H_{14} 1:1). Yield **15**, 0.14 g (0.56 mmol, 51%, brownish waxy solid). δ_H(300 MHz, $CDCl_3$) 8.21 (2 H, dd, *J* 7.6 and 1.8), 7.55 (4 H, m), 5.85 (2 H, d, *J* 1.1) and 5.56 (2 H, d, *J* 1.1); *m*/*z* (MS) 248 ($M^{\cdot +}$ with isotope pattern).

1,5-Diethynylnaphthalene (16). Selected spectral data taken from the ^{1}H NMR spectrum of the 700 °C pyrolysate (see text and Table 1). δ_H(300 MHz, $CDCl_3$) 8.40 (2 H, d, *J* 8.6), 7.78 (2 H, d, *J* 7.1), 7.53 (2 H, dd, *J* 8.6 and 7.1) and 3.50 (2 H, s, C≡C*H*); *m*/*z* (MS) 176 ($M^{\cdot +}$). The data are in agreement with those previously reported.[23]

5-(Trimethylsilylethynyl)acenaphthene (27). A deaerated solution of 2.0 g (7.8 mmol) of 5-bromoacenaphthene[25] and 1.61 g (16.4 mmol) of ethynyltrimethylsilane in 20 ml of anhydrous triethylamine was treated with 140 mg (0.2 mmol) of bis(triphenylphosphine)palladium dichloride and copper(I) iodide (10 mg, 0.05 mmol; for procedures, see ref. 26). The mixture was heated at reflux temperature overnight, cooled and subsequently filtered. The filtrate was concentrated giving **27** as an orange–brown waxy solid (0.50 g, 2.0 mmol, 26%). δ_H(300 MHz, $CDCl_3$) 7.88 (1 H, d, *J* 8.4, Ar), 7.64 (1 H, d, *J* 7.2, Ar), 7.53 (1 H, dd, *J* 8.4 and 6.9, Ar), 7.31 (1 H, d, *J* 6.9, Ar), 7.21 (1 H, d, *J* 7.2, Ar), 3.40 (4 H, m, cyclopentane unit) and 0.34 [9 H, s, Si(CH_3)$_3$].

5-Ethynylacenaphthene (5). Compound **27** (0.50 g, 2.0 mmol) was treated with 0.1 g of anhydrous potassium carbonate in methanol (30 ml) at room temperature for 3 h. After removal of the solvent under reduced pressure dichloromethane (60 ml) was added and the organic layer was washed with an aqueous sodium bicarbonate solution (30 ml). Subsequently, the organic layer was dried over magnesium sulfate and concentrated under reduced pressure. Pure **5** was obtained as an orange–brown waxy solid (0.21 g, 1.2 mmol, 60%). ν_{max}/cm^{-1} 3300 (≡*C*–*H*) and 2097 (–*C*≡CH); δ_H(300 MHz, $CDCl_3$) 7.93 (1 H, d, *J* 8.3, Ar), 7.69 (1 H, d, *J* 7.2, Ar), 7.55 (1 H, dd, *J* 8.3 and 6.8, Ar), 7.34 (1 H, d, *J* 6.8, Ar), 7.23 (1 H, d, *J* 7.2, Ar), 3.40 (4 H, m, cyclopentane unit) and 3.40 (1 H, s, $ArC{\equiv}CH$); δ_C(75 MHz, $CDCl_3$) 147.8, 146.3, 138.8, 133.0, 132.1, 121.0, 120.0, 118.8, 114.8, 81.9 and 80.5; *m/z* (MS) 178 ($M^{\cdot+}$).

5-(Trimethylsilylethynyl)acenaphthylene (28). A deaerated solution of 1.70 g (7.5 mmol) of 5-bromoacenaphthylene and 2.11 g (21.5 mmol) of ethynyltrimethylsilane in anhydrous triethylamine (40 ml) was treated with bis(triphenylphosphine)palladium dichloride (140 mg, 0.2 mmol) and copper(I) iodide (10 mg, 0.05 mmol; for procedures see ref. 26). The mixture was heated at reflux temperature overnight, cooled and subsequently filtered. The filtrate was concentrated giving **28** as a yellow waxy solid (0.43 g, 1.8 mmol, 24%). δ_H(300 MHz, $CDCl_3$) 8.07 (1 H, d, *J* 8.2, Ar), 7.72–7.56 (3 H, ABC system, *J* 7.1 and 6.8, Ar), 7.58 (1 H, dd, *J* 8.2, Ar), 7.07 and 6.99 (2 H, AB system, *J* 5.3, cyclopentene unit) and 0.36 [9 H, s, $Si(CH_3)_3$].

5-Ethynylacenaphthylene (8). Compound **28** (0.43 g, 1.74 mmol) was treated with 0.06 g of anhydrous potassium carbonate in methanol (30 ml) at room temperature for 3 h. After removal of the solvent under reduced pressure dichloromethane (60 ml) was added and the organic layer was washed with an aqueous sodium bicarbonate solution (30 ml). Subsequently, the organic layer was dried over magnesium sulfate and concentrated under reduced pressure. Pure **8** was isolated as a yellow waxy solid (0.17 g, 0.97 mmol, 56%). ν_{max}/cm^{-1} 3279 ($\equiv C$–H) and 2101 (–$C{\equiv}$CH); δ_H(300 MHz, $CDCl_3$) 8.11 (1 H, d, *J* 8.2, Ar), 7.75–7.56 (3 H, ABC system, *J* 7.1 and 6.8, Ar), 7.58 (1 H, d, *J* 8.2, Ar), 7.09 and 7.01 (2 H, AB system, *J* 5.3, cyclopentene unit) and 3.49 (1 H, s, $ArC{\equiv}CH$); δ_C(75 MHz, $CDCl_3$) 140.5, 139.8, 132.8, 130.7, 129.0, 128.8, 128.4, 128.2, 125.7, 124.7, 123.5, 120.0, 82.4 and 81.5; *m/z* (MS) 176 ($M^{\cdot+}$).

1,2-Dihydropyracylene (7).[1] Spectral data were taken from the ^1H NMR spectra of the 800–900 °C pyrolysates of **4** (see text and Table 3). δ_H(300 MHz, $CDCl_3$) 7.77 (2 H, d, *J* 6.9, Ar), 7.42 (2 H, d, *J* 6.9, Ar), 7.15 (2 H, s, cyclopentene unit) and 3.51 (4 H, s, cyclopentane unit); *m/z* (MS) 178 ($M^{\cdot+}$).

Pyracylene (1). Pure **1** is isolated from the 1100 °C pyrolysate according to the following procedure. The pyrolysate containing crude **1** is dissolved in CH_2Cl_2 (10 ml) and after evaporation of the solvent redissolved in pentane (0.01 g ml^{-1}). From this solution **1** crystallizes at -20 °C (overall yield 13% with respect to **4**). δ_H(300 MHz, $CDCl_3$) 6.64 (4 H, s, Ar) and 6.13 (4 H, s, cyclopentene unit); δ_C(75 MHz, $CDCl_3$) 142.0, 132.5, 131.7 and 124.9; *m/z* (MS) 176 ($M^{\cdot+}$). All analytical data are in agreement with those previously reported.[2]

1-(Trimethylsilylethynyl)acenaphthylene (29). A deaerated solution of 0.50 g (2.2 mmol) of 1-bromoacenaphthylene[27] and ethynylmethylsilane (0.40 g, 4.1 mmol) in anhydrous triethylamine (10 ml) was treated with bis(triphenylphosphine)palladium dichloride (30.8 mg, 0.04 mmol) and copper(I) iodide (2.2 mg, 0.01 mmol; for procedures see ref. 26). The mixture was heated at reflux temperature for 2 h, cooled and subsequently filtered. The filtrate was concentrated giving **29** as a viscous oil (0.39 g, 1.6 mmol, 73%). δ_H(300 MHz, $CDCl_3$) 7.82 (3 H, m, Ar), 7.68 (1 H, d, *J* 6.7, Ar), 7.57 (2 H, m, Ar), 7.26 (1 H, s, cyclopentene unit) and 0.33 [9 H, s, $Si(CH_3)_3$]; δ_C(75 MHz, $CDCl_3$) 139.2, 138.4, 133.5, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 124.9, 123.7, 123.4, 101.3, 100.1 and 0.1.

1-Ethynylacenaphthylene (23).[13] Compound **29** (0.32 g, 1.30 mmol) was treated with 0.1 g of anhydrous potassium carbonate in methanol (10 ml) at room temperature for 5 h. After removal of the solvent under reduced pressure dichloromethane (60 ml) was added and the organic layer was washed with an aqueous sodium bicarbonate solution (30 ml). Subsequently, the organic layer was dried over magnesium sulfate and concentrated under reduced pressure. Pure **23** was obtained as a yellow oil (0.15 g, 0.85 mmol, 65%). To prevent decomposition of **23** it has to be stored at -20 °C. ν_{max}/cm^{-1} 3300 ($\equiv C$–H) and 2100 (–$C{\equiv}$CH); δ_H(300 MHz, $CDCl_3$) 7.85 (3 H, m, Ar), 7.71 (1 H, d, *J* 7.6, Ar), 7.62 (1 H, dd, *J* 8.1 and 7.9, Ar), 7.57 (1 H, dd, 8.1 and 7.6, Ar), 7.34 (1 H, s, cyclopentene unit) and 3.49 (1 H, s, $C{\equiv}CH$); δ_C(75 MHz, $CDCl_3$) 139.0, 138.2, 134.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.2, 125.2, 123.4, 122.7, 83.2 and 79.0; *m/z* (MS) 176 ($M^{\cdot+}$).

3-Ethynylacenaphthylene (24). Selected spectral data taken from the ^1H NMR spectra of the 1100 °C pyrolysate (see text). δ_H(300 MHz, $CDCl_3$) 7.18 (1 H, d, *J* 5.8, cyclopentene unit), 7.07 (1 H, d, *J* 5.8, cyclopentene unit), 3.40 (1 H, s, $C{\equiv}CH$); *m/z* (MS) 176 ($M^{\cdot+}$). The data are in agreement with those previously reported.[13]

General flash vacuum thermolysis procedure for 5-(1-chloroethenyl)acenaphthene (4)

A commercial Thermolyne 21100 tube furnace containing an unpacked quartz tube (length 40 cm and diameter 2.5 cm) was used for all FVT experiments.[28] Temperature-conversion curves were determined by evaporating 0.1 g aliquots of **4** (evaporation temperature 85 °C and evaporation rate 0.3 g h^{-1}) into the quartz tube at a pressure of 10^{-2} Torr and the temperatures shown in Table 3. In the case of **2** and **15** also 0.1 g aliquots were used (10^{-2} Torr, evaporation temperature 120 °C and evaporation rate 0.3 g h^{-1}, see Tables 1 and 2). The product composition of all pyrolysates was determined by ^1H, ^{13}C NMR, GC, GC–MS and HPLC.

AM1 Calculations

Calculations were performed with AM1 as implemented in MOPAC 6.0.[14] Geometry optimization was executed without imposing any symmetry constraints using the keyword PRECISE. Transition states were located using an appropriate reaction coordinate and, subsequently, refined using the Eigenvector Following routine (keyword TS) until GNORM $\leqslant 0.5$. All minima and transition states were characterized by a Hessian calculation (keywords FORCE and LARGE); either none or only one imaginary vibration, respectively, was found. Heats of formation ($\Delta_f H^\circ$) of the minima and transition states (**TS**) are presented in the eqn. (1) and Schemes 1, 3 and 4. Both $\Delta_f H^\circ$ and activation enthalpies ($\Delta H^\ddagger$) are reported in kcal mol^{-1}.‡

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