Flow-Vacuum Pyrolysis of Polycyclic Compounds, 6[1]

Pyrolysis of Dibenzo $[CH]_8$ Hydrocarbons

Mircea D. Banciu*[a], Michaela D. Stanescu[a], Aurica Petride[b], Luminitza Parvulescu[a], and Mircea Pop[b]

Department of Organic Chemistry, Polytechnic University Bucharest[a],
Spl. Independentei 313, 76206-Bucharest (Roumania)

"C. D. Nenitzescu" – Institute of Organic Chemistry, Roumanian Academy[b],
Spl. Independentei 202 B, Bucharest (Roumania)

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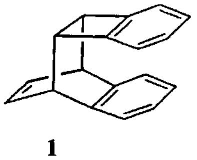
The flow-vacuum pyrolysis of dibenzo $[CH]_8$ hydrocarbons **2**, **3**, **4**, and **5** are studied at 1 Torr and in the temperature range between 400 and 650°C. The following new transformations have been observed: $\mathbf{2} \rightleftarrows \mathbf{4}$, $\mathbf{2} \rightarrow \mathbf{5}$, $\mathbf{3} \rightarrow \mathbf{5}$, $\mathbf{3} \rightleftarrows \mathbf{4}$, $\mathbf{3} \rightarrow \mathbf{2}$, $\mathbf{5} \rightarrow \mathbf{11}$, the last three presenting analogies in the $[CH]_8$ and/or benzo $[CH]_8$ series. A reaction mechanism is suggested.

In a previous paper[2] the thermal behavior of dibenzo $[CH]_{10}$ hydrocarbon **1** (*syn*-dibenzo[*c*,*g*]Nenitzescu hydrocarbon) was investigated. Two of its reaction products, **2** and **3**, were dibenzo $[CH]_8$ hydrocarbons. Whereas the formation of **2** could be easily rationalized due to the formation of a benzocyclobutadiene intermediate (generated by a retrodiene reaction of **1**), the occurrence of **3** seemed to be a consequence of a further thermal conversion of **2** which has previously not been described.

Thus, a more detailed investigation of the thermal behavior of dibenzo $[CH]_8$ hydrocarbons seems to be of interest. From the 17 theoretically possible dibenzo $[CH]_8$ hydrocarbons[3] – including five structures corresponding to separable graphs[3] and three containing less stable quinonoid structures – only eight are presently known, namely: 6a,10b-dihydrobenzo[*a*]biphenylene (Cava dimer of benzocyclobutadiene) (**2**); dibenzo[*a*,*e*]cyclooctene (dibenzo-COT) (**3**); 4b,8b,8c,8d-tetrahydrodibenzo[*a*,*f*]cyclopropa[*c*,*d*]pentalene (Pettit hydrocarbon) (**4**); 9,10-dihydro-9,10-ethenoanthracene (Cristol hydrocarbon) (**5**); dibenzo[*c*,*g*]tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (Nenitzescu dimer of benzocyclobutadiene) (**6**); 2a,10b-dihydrocyclobuta[*l*]phenanthrene (**7**); dibenzo[*a*,*c*]cyclooctene (**8**), and the unstable quinonoid hydrocarbon **9** (dihydrobenzo[*b*]biphenylene). In contrast to the thorough investigation of the photochemistry of dibenzo $[CH]_8$ hydrocarbons[4,5], only two thermal conversions are known in this series of compounds: isomerization of **6** to **3** via **9**, discovered in this laboratory in 1959[6], and ring opening of **7** to **8**, described by Vogel in 1963[7]. In this paper the results of the yet undescribed flow-vacuum pyrolysis of the remaining hydrocarbons **2**, **3**, **4**, and **5** are discussed.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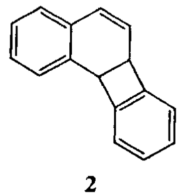
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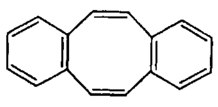
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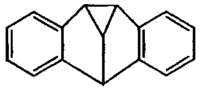
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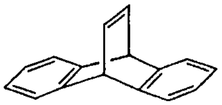
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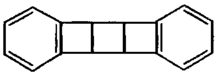
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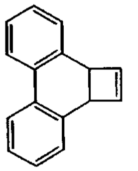
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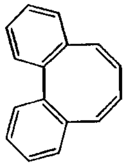
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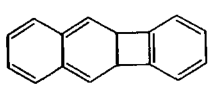
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Results

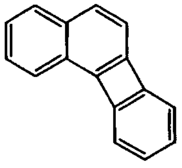
The syntheses of dibenzo $[CH]_8$ hydrocarbons **2**–**5** were performed according to literature procedures (see Experimental). The flow-vacuum pyrolyses of these hydrocarbons were realized in a constant argon stream at 1 Torr and in the temperature range between 400 and 650°C (700°C). The calculated contact times were about 0.25 s. The crude reaction products (representing about 95% at 400°C and 85% at 650°C) were analyzed by GLC using two different columns. The reaction products were identified by a comparison with authentic samples. In some cases, LC was also used in order to separate the reaction products on a preparative scale.

The distribution of the pyrolysis products of **2-5** as a function of temperature is indicated in Figures 1–4.

On the basis of the experimental results the following conclusions can be drawn:

1) *Pyrolysis of the Cava Dimer* **2** (Figure 1)

- The product distribution is the most complex among all investigated hydrocarbons.
- The first pyrolysis product of **2** is the Pettit hydrocarbon **4** (reaching a maximum of ≈35% at 530 °C).
- At somewhat higher temperatures dibenzo-COT **3** appears (very probably at the expense of **4**) and reaches a maximum of 27% at about 575 °C.
- A pattern relatively similar to that of **3** is indicated by hydrocarbon **5**; however, this hydrocarbon reaches at 575 °C a maximum of only 12%.
- Two highly aromatized hydrocarbons generated at > 550 °C become the main reaction products at temperatures above 600 °C: benzo[*a*]biphenylene (**10**) and anthracene (**11**).



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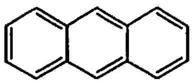

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2) *Pyrolysis of Dibenzo-COT* **3** (Figure 2)

- Hydrocarbon **3** is thermally more stable than **2**.
- The first pyrolysis product is the Pettit hydrocarbon **4**, appearing, however, in small amounts (10–11% at 550–600 °C).
- Cava dimer **2** was identified in very small amounts (1–2% at 450–550 °C; not shown in Figure 2). At temperatures higher than 550 °C hydrocarbon **2** disappears along with the occurrence and a strong increase of the amount of aromatized hydrocarbon **10** (reaching 55% at 700 °C).
- Small amounts of Cristol hydrocarbon **5** are formed at higher temperatures (7.5% at 650 °C) being subsequently removed due to the formation of anthracene (**11**) on further increase of temperature.

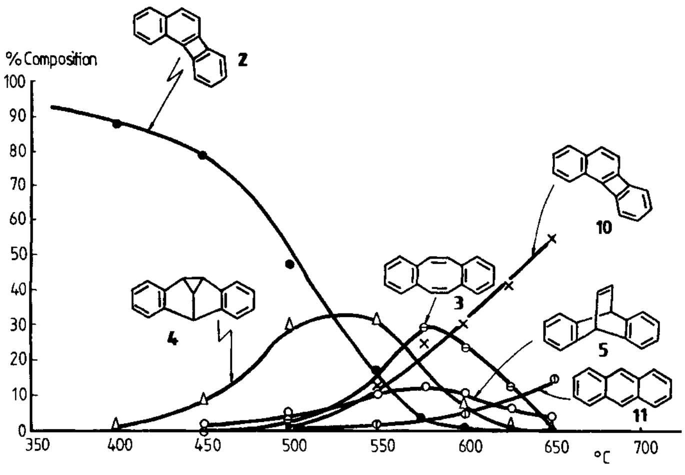


Figure 1. Product distribution in the flow-vacuum pyrolysis of hydrocarbon **2** (1 Torr; Argon flow-rate 4 ml min^{-1})

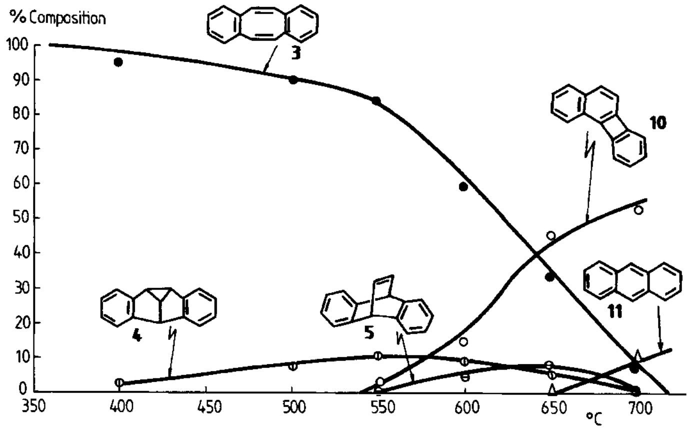


Figure 2. Product distribution in the flow-vacuum pyrolysis of hydrocarbon **3** (1 Torr; Argon flow-rate 4 ml min^{-1}). Small amounts (1–2%) of the Cava hydrocarbon **2** were also observed between 450 and 550 °C (not shown)

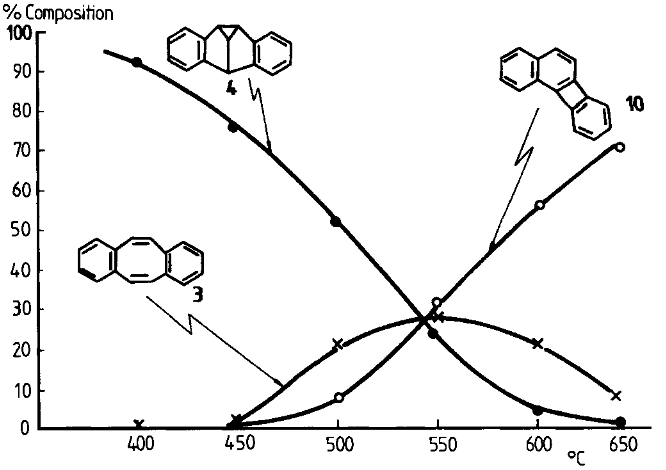


Figure 3. Product distribution in the flow-vacuum pyrolysis of hydrocarbon **4** (1 Torr; Argon flow-rate 4 ml min^{-1}). Small amounts of hydrocarbons **2** and **5** (1–2.5% each) were also observed between 450–550 °C (not shown)

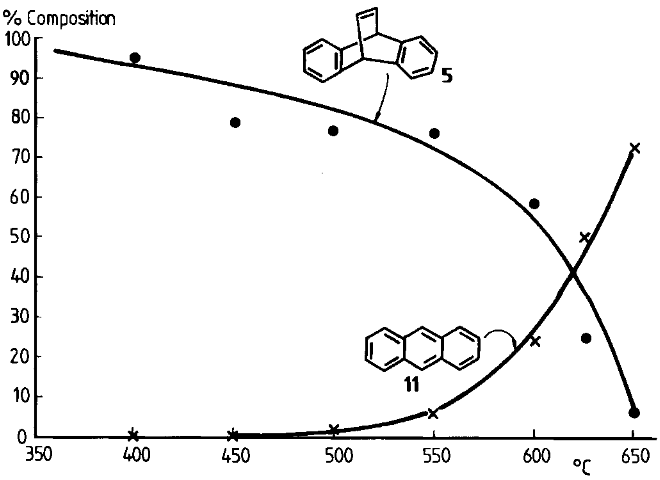
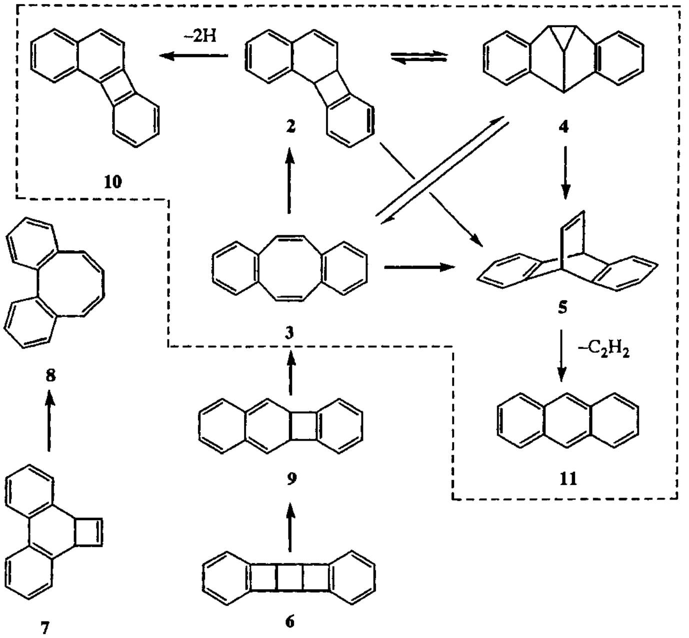


Figure 4. Product distribution in the flow-vacuum pyrolysis of hydrocarbon **5** (1 Torr; Argon flow-rate 4 ml min^{-1})

Scheme 1. Thermal transformations in the dibenzo $[CH]_8$ hydrocarbon series (the new conversions are enclosed by dotted lines)



3) *Pyrolysis of Pettit Hydrocarbon* **4** (Figure 3)

- A clean conversion of hydrocarbon **4** into dibenzo-COT (**3**) is noticed starting at 450 °C. The maximum yield of **3** is 28% at about 550 °C.
- Small amounts of **2** and **5** (1 – 2.5% each; not shown in Figure 3) are generated between 450 and 550 °C disappearing at higher temperatures.
- Above 550 °C benzo[*a*]biphenylene (**10**) is formed in large amounts simultaneously with the rapid disappearance of both **4** and **3**. At 650 °C **10** represents 70% of reaction mixture.

4) *Pyrolysis of Cristol Hydrocarbon* **5** (Figure 4)

- A clean unimolecular conversion of **5** into anthracene (**11**) is observed in the temperature range of 400 – 650 °C. However, the thermal stability of **5** is remarkable: at 550 °C only 25% conversion is noticed under the reaction conditions.

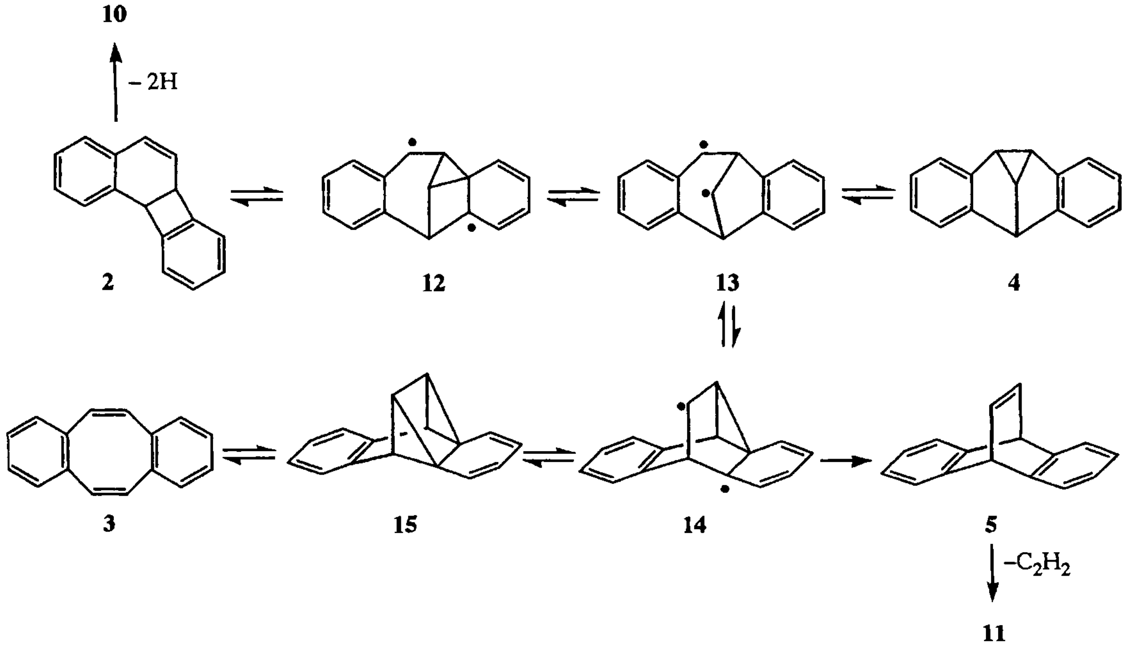
Discussion

The new thermal reactions occurring in the above mentioned experiments are collected in Scheme 1 along with the previously known ones[6,7].

Though various thermally allowed concerted steps could be suggested in the explanation of these transformations, the generation of free radicals seems to be highly favored under the reaction conditions used (gaseous phase, elevated temperatures). Diradical intermediates were suggested in some thermal conversions of $[CH]_8$ hydrocarbons[8–11]. Another hint in this context comes out from the paper of Adam and coworkers[5] who, suggesting radicalic intermediates in the generation of **2** – **5** from suitable azoalkanes, demonstrated also that hydrocarbons **2** – **5** do not undergo thermal interconversions up to 170 – 200 °C in a static system or at 275 °C in a flow system (conditions favouring concerted processes). Thus, in order to explain the reactions of the same hydrocarbons occurring above 400 °C the following rationalizations (Scheme 2) are advanced:

The main intermediates specified in this scheme are the same as proposed by Adam[5], the difference being however that in the observed interconversions the equilibration of the intermediates **12** – **15** and their corresponding hydrocarbons were also suggested. The interconversions of intermediates **12** – **15** usually involve radicalic transformations whereas the interconversion **3** ⇄ **15** is a thermally allowed [2 + 2 + 2] cycloaddition/cycloreversion. The high temperatures used may explain the loss of benzene aromaticity

Scheme 2



in the formation of **12** and **14**. The thermal reactions affording **5** remain irreversible because **5** is converted (due to the liberation of acetylene) into anthracene (**11**) by a retrodiene reaction. Similarly, at elevated temperatures **2** is irreversibly converted into its dehydro derivative, i.e. the stable aromatic compound **10**.

A comparison of the data from Figures 1 – 4 permits the following order of thermal stability to be established: **2** < **4** < **3** < **5**.

In summary, according to Scheme 1 the following new transformations are disclosed: thermal interconversion **2** $\rightleftarrows$ **4**; thermal conversions **2** $\longrightarrow$ **5** and **3** $\longrightarrow$ **5**. Some other thermal reactions representing analogies in the $[CH]_8$ and/or benzo $[CH]_8$ series are demonstrated in this paper for dibenzo $[CH]_8$ hydrocarbons, namely interconversion **3** $\rightleftarrows$ **4** (by analogy with substituted hydrocarbons from $[CH]_8$ series[8,9]), conversion **3** $\longrightarrow$ **2** (by analogy with the $[CH]_8$[12] and benzo $[CH]_8$ series[13]), and decomposition **5** $\longrightarrow$ **11** (by analogy with the $[CH]_8$[14] and benzo$[CH]_8$ series[15]). It should be also added that the previously described rearrangement **6** $\longrightarrow$ **3**[6] has meanwhile found analogies in the $[CH]_8$[16] and benzo $[CH]_8$ series[17].

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Experimental

Melting Points (uncorrected): Boetius apparatus. – IR (KBr): C. Zeiss-UR 20. – UV: C. Zeiss-Specord UV-Vis. – ^{1}H NMR: Gemini 300 Varian, TMS as internal standard. – GLC analyses: Fractovap 2450 C. Erba apparatus, FID detector, capillary-fused silica columns with SE-52- and/or SE-54 silicon polymer; length 25 m, internal diameter 0.35 mm; temperature program: 100 – 200°C at 5°C min^{-1}, then 200 – 260°C at a heating rate of 10°C min^{-1}; carrier gas: hydrogen; flow rate 1 ml min^{-1}; volatilization temperature 275°C.

Syntheses of Hydrocarbons **2** – **5**

6a,10b-Dihydrobenzo[a]biphenylene (**2**) was synthesized according to the method of Nenitzescu et al.[18] starting by treatment of 1,2-dibromobenzocyclobutene with Li/Hg (75% yield); m. p. 74°C (from ethanol); GLC purity 95%. IR and ^{1}H-NMR spectra as previously reported[2].

Dibenzo[a,e]cyclooctene (**3**) was prepared by reaction of 1,2-dibromobenzocyclobutene with $Ni(CO)_4$ followed by thermal retrocyclization of intermediate **6**[6b]; white solid, 50% yield; m. p. 108 – 109°C (from ethanol); GLC purity 98%. The IR[19] and ^{1}H-NMR[20] spectral data were identical with those reported in the literature.

4b,8b,8c,8d-Tetrahydrodibenzo[a,f]cyclopropa[c,d]pentalene (**4**): The photoisomerization of hydrocarbon **5** in acetone solution according to Ciganek[4a] gave compound **4** in 70% yield; m. p. 105°C (from ethanol); GLC purity 96%. – ^{1}H-NMR spectral data were as reported in ref.[21]

9,10-Dihydro-9,10-ethenoanthracene (**5**): Application of the Grob oxidation[22] to 9,10-dihydro-9,10-ethanoanthracen-11,12-dicarboxylic acid afforded the hydrocarbon **5** in 45% yield; m. p. 119 – 120°C (from ethanol); GLC purity 97.5%. – ^{1}H-NMR spectral data were as reported in ref.[23]

Flow-Vacuum Pyrolyses of Hydrocarbons **2** – **5** were performed in a pyrolysis apparatus equipped with a vertical quartz tube (length 60 cm, inner diameter 1 cm, filled at 30 cm height with quartz chips), a cylindric electric oven, a thermocouple, a McLeod vacuum manometer, devices for inert gas (argon) flow-rate measurement, a vacuum source ($\leqslant$ 1 Torr) and a cooled receiver vessel. For analytical purposes 30-mg samples of hydrocarbons **2** – **5** were pyrolyzed at 1 Torr at an argon flow rate of 4 ml min^{-1} and in the temperature range between 400 and 650°C (700°C); calculated contact times $\leqslant$ 0.25 s. The crude pyrolyzates solidifying at the cold lower end of the pyrolysis tube were dissolved in CH_2Cl_2. The obtained solutions were filtered, then the solvent was evaporated in vacuo. The solid residues – obtained in yields which vary between 95% (28.5 mg) at 400°C and 85% (25.5 mg) at 650°C – were subsequently subjected to GLC analysis. The results of VPC analyses of the crude pyrolyzates of **2** – **5** are graphically presented in Figures 1 – 4. The differences up to 100% composition were due to numerous minor nonidentified components.

In preparative pyrolyses 50-mg samples were used, the products of five identical runs being collected.

The crude product of the pyrolysis of **2** at 525°C (200 mg; 80%) was chromatographed on a silica column (Merck 60 reinst, 0.063 – 0.200 mm, 70 – 230 mesh, length 50 cm, diameter 1 cm) with petroleum ether (b. p. 35°C) as the eluent, the order of eluted compounds being **3**, **2**, and **4**.

The hydrocarbons **3** (17.5 mg; 7%), **2** (62.5 mg; 25%), and **4** (70 mg; 28%) were further identified by a comparison of their melting points, IR and ^{1}H-NMR spectra with those of authentic samples.

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