

## Flow-vacuum pyrolysis of 5H-10,11-dihydro-dibenzo[a,d]-cyclohepten-5-ol and 5-hydroxymethyl-5H-dibenzo[a,d]-cycloheptene

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### Abstract

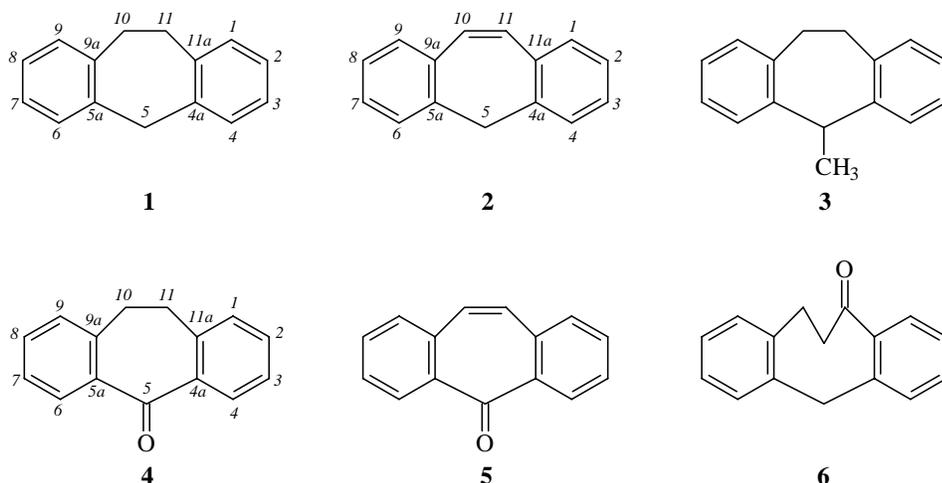
Flow-vacuum pyrolysis of title compounds **7** and **8** was investigated at 1.33 mbar on a large temperature interval (500°C-800°C). The main reaction products of **7** were: anthracene, 9-methylanthracene, dibenzosuberone, 5H-dibenzo[a,d]cycloheptene and 5H-10,11-dihydro-dibenzo[a,d]cycloheptene. The pyrolysis products of **8** were: anthracene, 9-methyl-anthracene, phenanthrene, 5H-dibenzo[a,d]cycloheptene and 5-methylene-5H-dibenzo[a,d]cycloheptene. Radical mechanisms are proposed for rationalization of the formation of above products. A comparison of reaction routes in pyrolyses of the title alcohols is presented. The results are also compared with those of previously studied dynamic pyrolyses of related hydrocarbons and ketones.

**Keywords:** Flow-vacuum pyrolysis, dibenzocycloalkanols, radicals, carbenes

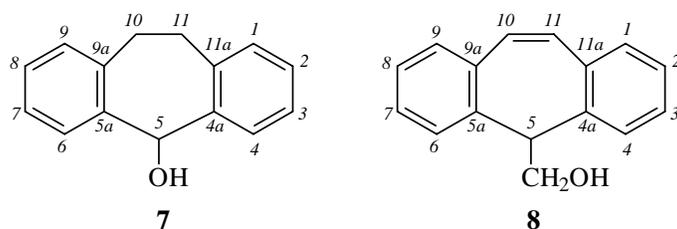
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### Introduction

Continuing our researches in flow-vacuum pyrolysis of benzoannelated cyclic and polycyclic compounds<sup>1</sup> we described recently the thermal behavior of some related dibenzocycloalkanes **1**<sup>2</sup>, **2**<sup>2</sup>, **3**<sup>3</sup> and dibenzocycloalkanones **4**<sup>4</sup>, **5**<sup>4</sup>, **6**<sup>5</sup>. During these works we evidenced some interesting rearrangement- and aromatization processes conducting finally mainly to anthracene, methylanthracenes and phenanthrene.



In the present work we studied the pyrolysis of two related dibenzocycloalkanols **7** and **8** in order to compare their product distributions and reaction mechanisms.

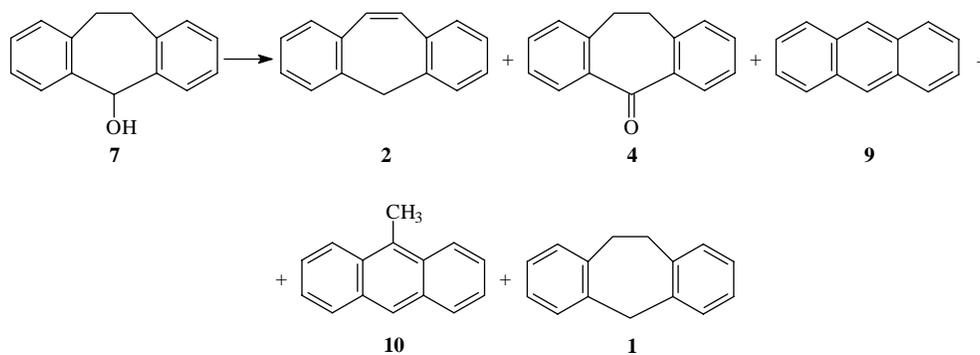


It was assumed that a useful comparison could be also made with the previously investigated hydrocarbons and ketones in order to prove the possible similarities of the reaction mechanisms. The structure and properties of the final aromatic hydrocarbon products can be also of some interest in connection with the environmental problems aroused by incineration of organic waste materials.

## Results

The alcohol **7** was obtained by reduction of dibenzosuberone **4**<sup>6</sup> whereas the alcohol **8** was prepared using our previously described procedure<sup>7</sup> including the formolysis of 9,10-bis(hydroxymethyl)-9,10-dihydroanthracene ditosylate followed by alkaline hydrolysis. All pyrolyses of the alcohols **7** and **8** were performed in a quartz flow-system under argon atmosphere at 1.33 mbar, the calculated contact times being less than 0.2s. The distribution of the reaction products was followed using GC/MS. The major products were isolated by liquid chromatography and subsequently spectrally analyzed.

The products formed in the pyrolysis of **7** are presented in the following equation and their distribution versus temperature (500°-800°C) in Figure 1a.



Hydrocarbons **2**, **9** and **10** appear also in the pyrolyses of the alcohol **8** (500°-875°C) but, in this case, instead of **4** and **1**, the hydrocarbons **11** and **12** were formed (see also Figure 1b).

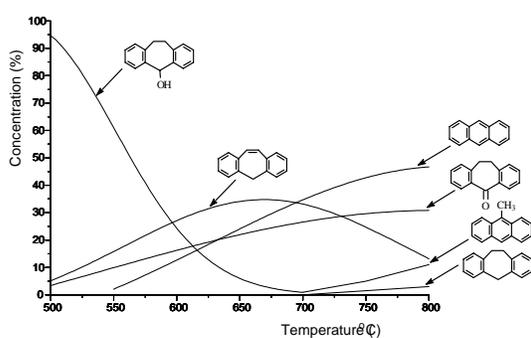
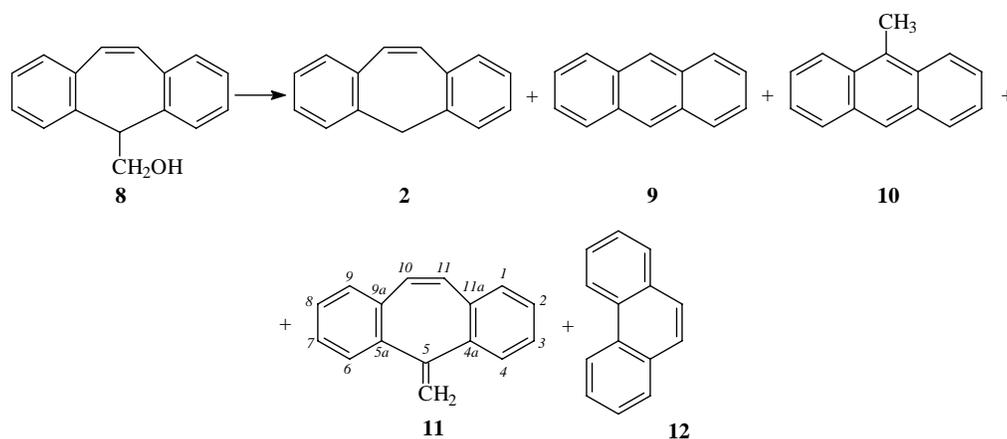


Fig. 1a

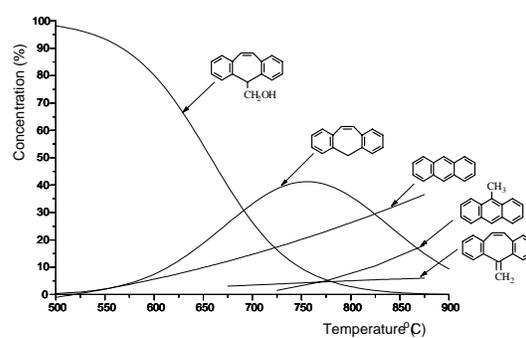


Fig. 1b

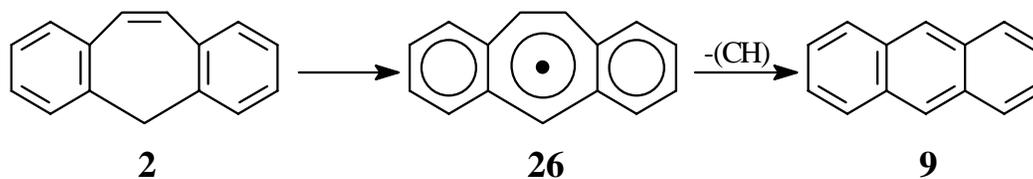
**Figure 1.** Product distribution versus temperature in the pyrolyses of alcohols **7** (Figure 1a) and **8** (Figure 1b); (1.33 mbar; argon flow-rate 4 mL·min<sup>-1</sup>; small amounts, 1-2%, of anthraquinone, in the case of **7**, and of phenanthrene, anthraquinone and 5,5'-bis-5H-dibenzo[a,d]cycloheptenyl in the case of **8** were not presented in Figures).

Liquid chromatography permitted the separation of **9**, **2**, **1** and **4** from pyrolysis products of **7** and of **9**, **2** and **11** from pyrolysis products of **8**. All the separated products indicated identical spectral data and chromatographic retention times with authentic specimens.

## Discussion

The experimental data presented above show that the thermal decomposition of alcohol **7** between 500°C and 700°C afforded three main products: dibenzosuberone (**4**), anthracene (**9**) and 5*H*-dibenzo[*a,d*]cycloheptene (**2**). The increasing amounts of these compounds in parallel with disappearance of **7** suggest their direct formation from alcohol **7**. A further increase of pyrolysis temperature over 700°C (domain in which **7** disappeared from reaction mixture) permitted the observation of the following facts: (i) a further increase of anthracene content; (ii) formation of 9-methylanthracene (**10**) and of saturated hydrocarbon **1** on the expense of **2**. As it was proved by our group the authentic hydrocarbon **2**<sup>8</sup> is thermally converted in FVP over 650°C into anthracene and 9-methylanthracene.<sup>2</sup> On the basis of the above considerations a possible reaction mechanism for pyrolysis of **7** is presented in Scheme 1. The mechanism included three parallel radical reaction routes. The radical mechanisms are favoured by the reaction conditions: quartz apparatus, gaseous phase, high temperatures. The route (*a*) describes the sequential loss of two hydrogen atoms affording the ketone **4**. Formation of ketones in pyrolysis of secondary alcohols is well-known.<sup>9</sup> The second route (*b*) includes the homolytic break of C-OH bond conducting to relatively stable mesomeric benzylic radical **14**, followed by a H· loss affording the hydrocarbon **15** from which the isolable hydrocarbon **2** can occur by a thermally allowed 1.5H-migration. It is worth mentioning here that hydrocarbon **15** was trapped by Pomeranz<sup>10</sup> during *static* pyrolyses of **2**. On the other hand the thermally allowed disrotatory conversion **15**→**16**, followed by usual radical steps can produce 9-methylanthracene (**10**). Hydrocarbon **1**, occurring in small amounts at high temperature, is a hydrogenation product of **2** with hydrogen atoms formed in different steps of the mechanism. In the route (*c*) by homolytic break of the central CH<sub>2</sub>-CH<sub>2</sub> bond of **7** the stable benzylic mesomeric diradical **19** can be formed. Cyclization of **19** can conduct to two enantiomeric spiranes **20** and **22**. In agreement with Trahanovsky's mechanism suggested for related compounds<sup>11</sup> and by our take into consideration of such enantiomeric spiranes<sup>5</sup> the compounds **20** and **22** can equilibrate with bridged diradicals **21** respectively **23**.

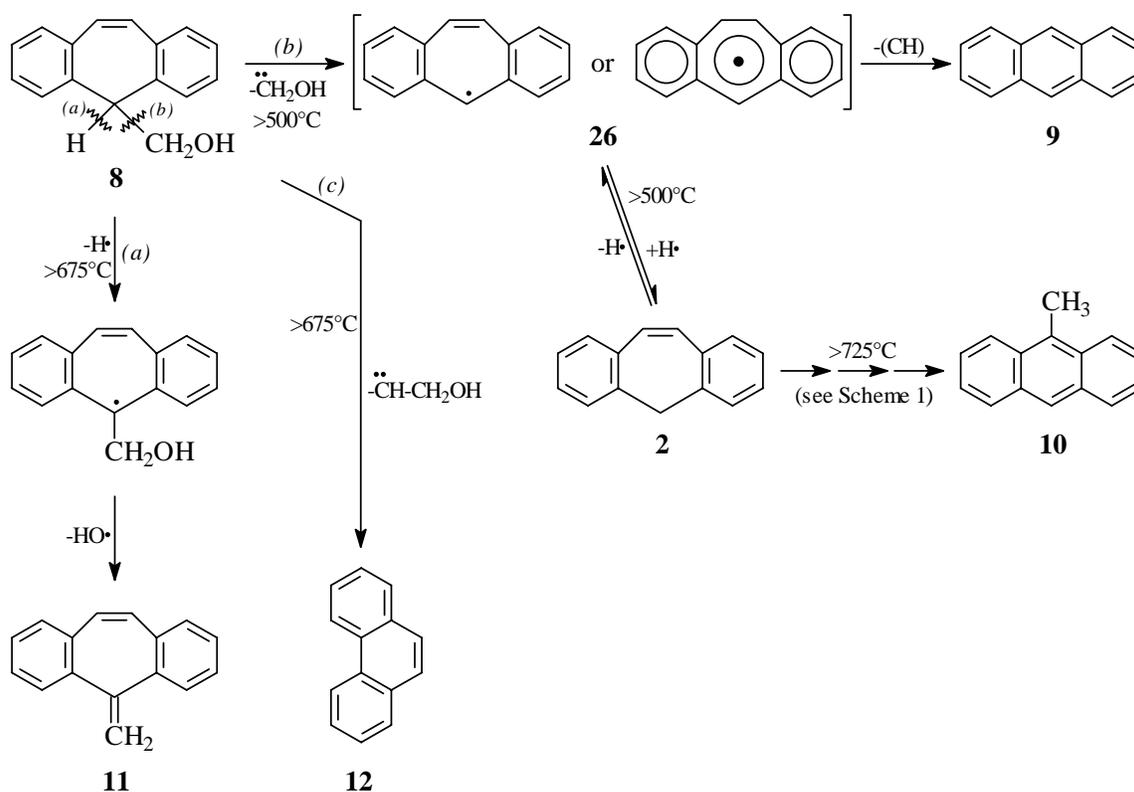
Thermal elimination of bridges (most probably as carbene fragments) leads to anthracene derivatives **24**, respectively **25** which are easily thermally aromatized to anthracene (**9**). Finally it should be mentioned that the conversion of **2** into anthracene (**9**), observed by us<sup>2</sup> as a minor route in dynamic pyrolyses of **2** and by Pomeranz<sup>10</sup> as a major route in static pyrolyses of the same hydrocarbon, was explained<sup>10</sup> *via* the dibenzotropylium radical **26** which losses a CH unit (with unelucidated structure).



The results of the pyrolysis of primary alcohol **8** (Figure 1b) indicated the formation at lower temperatures (500°-675°C) of only two products on the expense of starting material, namely 5*H*-dibenzo[*a,d*]cycloheptene (**2**) and anthracene (**9**). The increase of the reaction temperature has as effects: (i) formation of increasing amounts of anthracene; (ii) formation of 9-methyl-anthracene (**10**) (starting from 725°C); (iii) formation of small amounts of methylenic hydrocarbon **11** and phenanthrene (**12**) (not presented in Figure 1b); (iv) decrease of concentrations of the starting material (at 775°C it disappears from the reaction products) and of hydrocarbon **2**. All these facts can be explained taking into account the reaction mechanism suggested in Scheme 2.



hydrocarbon **2** and following the steps suggested in Scheme 1 the 9-methylantracene (**10**) is generated (over 725°C). On the other hand, over 675°C the dehydration product **11** can be formed in two successive steps (route *a*) along with phenanthrene (**12**) (route *c*). The very high thermal stability of methylenic hydrocarbon **11** was proved by a control experiment with a pure sample of **11** which indicated a conversion of only ~10% at 800°C. Comparing the pyrolyses of **7** and **8** it can be easily observed that: (i) the break of the middle ring is inoperative in the case of **8** due to the presence of a C=C double bond whereas in the case of **7** this step constitutes a major route due to the single bond character of the central C-C bond; (ii) the dehydrogenation to carbonyl compounds, another major route at the secondary alcohol **7**, is missing at the primary alcohol **8** where the presumptive product would be an unstabler aldehyde. Along with these differences a similarity of behavior could be also noticed: the hydrocarbon **2** reaches its maximum amount right when the starting material **7** or **8** disappeared among the reaction products (700°C for **7** and 775°C for **8**). This experimental fact proves, besides the differences in thermal reactivity of secondary and primary alcohols, the initial formation of **2** from both starting materials, in agreement with the suggested mechanisms.



**Scheme 2.** Pyrolysis mechanism of **8**.

## Conclusions

- The alcohols **7** and **8** add to the previously investigated compounds **1**<sup>2</sup>, **2**<sup>2</sup>, **3**<sup>3</sup>, **4**<sup>4</sup> and **6**<sup>5</sup> affording anthracene as major pyrolysis product.
- Trahanovsky's mechanism including spiranes and bridged diradicals<sup>11</sup> can be applied to saturated alcohol **7** also. The mechanism was extended taken into consideration enantiomeric spiranes.
- The main intermediate is in both cases the isolable hydrocarbon **2**, converted at higher temperatures into anthracene and 9-methylanthracene.
- Whereas in the case of secondary alcohol **7** (totally converted at 700°C) an important by-product is the corresponding ketone **4**, the primary alcohol **8** (totally converted at 775°C) affords the methylenic hydrocarbon **11** and phenanthrene as minor products.

## Acknowledgements

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## Experimental Section

**General Procedures.** IR spectra were taken on a IR-Bruker-EQUINOX 55 spectrophotometer. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra ( $\delta$  ppm, CDCl<sub>3</sub> as solvent, TMS as internal standard) were recorded on a Varian Gemini 300 instrument at 300 MHz (<sup>1</sup>H) and 75 MHz (<sup>13</sup>C). The UV spectra were recorded on a SPECORD UV/VIS Carl Zeiss Jena double beam spectrometer. Elemental analyses were carried out on a Carlo Erba Model 1106 Elemental Analyser. The GC/MS analyses were performed on a Varian 3400 gas-chromatograph with split/splitless injector, coupled with a Varian Saturn II mass spectrometer provided with ion trap. A capillary DB-5 column (30 m long, 0.25 mm internal diameter) was used. The analysis conditions were as follows: injector temperature, 250°C; split rate, 1:60; temperature program, 60-250°C with a heating rate of 10°C·min<sup>-1</sup>; carrier gas, helium (1 mL·min<sup>-1</sup>); temperature of transfer-line, 250°C; electron ionization, 70 eV.

**Preparative column chromatography.** The reaction mixtures (about 250 mg) from preparative pyrolyses of **7** (at 750°C) and **8** (at 850°C) were chromatographed on a SiO<sub>2</sub> (Merck, 70-230 mesh) column (17 mm diameter, 24 cm SiO<sub>2</sub> layer height) using pentane as solvent. From the products of **7** the isolated compounds (in the order of their elution) were: **9**, **2**, **1**, **4** whereas from the products of **8** they were: **9**, **2**, **11**.

### General procedure for pyrolysis experiments

All vacuum pyrolyses were performed in a flow system using a previously described apparatus<sup>4</sup>. The pyrolysis quartz tube (60 cm length, 10 mm diameter) was filled with quartz chips on 30 cm length; this zone was heated with a cylindrical electric oven. The temperature was measured by means of a thermocouple and the pressure (1.33 mbar) with a McLeod manometer. The alcohol sample (usually 30 mg) was sublimed under argon flow (4 mL·min<sup>-1</sup>) in the pyrolysis tube. The reaction products accumulated at the cooled end of the quartz tube were dissolved in chloroform, the solvent was evaporated *in vacuo* and the residual solid was subjected to GC/MS analysis. Analytical pyrolyses were followed by preparative runs (combining the products of more identical experiments for each alcohol) allowing the isolation of the main products by column chromatography.

### Starting materials

**5H-10,11-Dihydro-dibenzo[*a,d*]cyclohepten-5-ol (7)** was prepared according to lit.<sup>6</sup> mp 108°C (lit.<sup>6</sup> mp 92-3°C). <sup>1</sup>H-NMR (300 MHz): δ=7.46 (m, 2H, H-4, H-6), δ=7.18-7.29 (m, 6H, H-1-3, H-7-9), δ=3.43 (m, 2H, H-10, H-11), δ=3.12 (m, 2H, H-10', H-11').

<sup>13</sup>C-NMR: δ=140.45 (C-4a, C-5a), 138.83 (C-9a, C-11a), 130.12\* (C-2, C-8), 127.88\* (C-1, C-9), 126.98 (C-4, C-6), 126.11 (C-3, C-7), 76.95 (C-5), 32.33 (C-10, C-11). IR (KBr), ν/cm<sup>-1</sup> 3328 (wide, assoc. OH), 3066, 3018, 2937, 2901, 1484, 1457, 1356, 1182, 1033, 778, 753, 721. MS, m/e %: 212 (M+2, 3), 211 (M+1, 15), 210 (M, 30), 209 (13), 195 (10), 194 (10), 193 (20), 192 (BP, 100), 191 (28), 190 (7), 189 (9), 181 (11), 180 (2), 179 (13), 178 (24), 177 (4), 176 (4), 167 (3), 166 (8), 165 (28), 153 (3), 152 (12), 133 (44), 132 (9), 131 (4), 128 (4), 105 (12), 104 (4), 103 (10), 96 (10), 94 (13), 91 (40), 90 (10), 89 (11), 83 (6), 82 (13), 78 (4), 77 (12), 76 (6), 65 (6), 63 (5). UV (MeOH), λ<sub>max</sub> nm, lg ε<sub>max</sub>: 212 (4.19), 264 (1.87). Anal. calcd. for C<sub>15</sub>H<sub>14</sub>O (210.27): C, 85.68; H, 6.71. Found: C, 85.90; H, 6.50%.

**5-Hydroxymethyl-5H-dibenzo[*a,d*]cycloheptene (8)** was prepared according to Nenitzescu et al<sup>7</sup>, mp 86-7°C (lit.<sup>7</sup> mp 86-7°C). <sup>1</sup>H-NMR (300 MHz): δ=7.25-7.38 (m, 8H, H-arom), δ=6.85 (s, 2H, H-10, H-11), δ=4.20 (t, 1H, H-5, J<sub>5,12</sub>=8 Hz), δ=3.81 (d, 2H, H-12, J<sub>12,5</sub>=8 Hz). In the presence of Eu(fod)<sub>3</sub>/sample=0.25 molar ratio the above spectrum becomes: δ=8.16 (dd, 2H, H-4, H-6, J<sub>4(6), 3(7)}</sub> = 7.5 Hz, J<sub>4(6), 2(8)}</sub> = 1.3 Hz), δ = 7.72 (ld, 2H, H-1, H-9, J<sub>1(9), 2(8)}</sub> = 7.5 Hz, J<sub>1(9), 3(7)}</sub> = 1.5 Hz), δ=7.60 (td, 2H, H-3, H-7, J<sub>3(7), 4(6)}</sub> = 7.5 Hz, J<sub>3(7), 1(9)}</sub> = 1.5 Hz), δ=7.51 (td, 2H, H-2, H-8, J<sub>2(8), 1(9)}</sub> = 7.5 Hz, J<sub>2(8), 4(6)}</sub> = 1.3 Hz), δ = 7.43 (s, 2H, H-10, H-11), δ=7.35 (ls, 2H, H-12), δ=6.40 (lt, 1H, H-5). <sup>13</sup>C-NMR: δ=137.60 (C-4a, C-5a), 134.31 (C-9a, C-11a), 130.72 (C-4, C-6, C-10, C-11), 129.95 (C-1, C-9), 128.96 (C-3, C-7), 127.05 (C-2, C-8), 61.09 (C-12), 57.99 (C-5). IR (KBr), ν/cm<sup>-1</sup>: 3268 (wide, assoc. OH), 3056, 3018, 2937, 2903, 2882, 1492, 1460, 1433, 1160, 1043, 947, 883, 799, 761, 744, 728. MS, m/e %: 223 (M+1, 0.5), 222 (M<sup>+</sup>, 4.0), 193 (2), 192 (12), 191 (BP, 100), 189 (24), 187 (3), 178 (2), 176 (2), 165 (15), 163 (3), 152 (2), 139 (2), 115 (2), 95 (2), 82 (2), 81 (2), 63 (2). UV (MeOH), λ<sub>max</sub> nm, lg ε<sub>max</sub>: 211 (4.45), 227 (4.38),

\* The attributions may be interchanged

238.5 sh (4.04), 294 (4.17). Anal. calcd. for C<sub>16</sub>H<sub>14</sub>O (222.28): C, 86.45; H, 6.35. Found: C, 86.26; H, 6.47%.

### Pyrolysis products

Pyrolysis products of alcohol **7** were: **2**, **4**, **9**, **10** and **1**, whereas the products of **8** were: **2**, **9**, **10**, **11** and **12**. From these, anthracene (**9**), 9-methylanthracene (**10**) and phenanthrene (**12**) were identified through their well-known spectral data as well as by mixed samples with pyrolysis products in GC. The physical data of **2**, **4**, **1** and **11** (completing and/or updating the older ones) are given below.

**5H-Dibenzo[*a,d*]cycloheptene (2).** mp 132°C (lit.<sup>8</sup> mp 132°C). <sup>1</sup>H-NMR (300 MHz): δ=7.15-7.33 (m, 8H, H-1-4, H-6-9), δ=7.01 (s, 2H, H-10, H-11), δ=3.73 (s, 2H, 2H-5).

<sup>13</sup>C-NMR: δ=138.12 (C-4a, C-5a), 135.17 (C-9a, C-11a), 131.52 (C-10, C-11), 128.40\* (C-4(1), C-6(9)), 128.10\* (C-1(4), C-9(6)), 127.87 (C-2, C-8), 126.05 (C-3, C-7), 41.63 (C-5). IR (KBr), ν/cm<sup>-1</sup>: 3057, 3025, 2961, 2885, 2830, 1955, 1489, 1438, 1261, 1157, 1098, 1037, 951, 892, 814, 801, 762, 735, 704. MS, m/e %: 194 (M+2, 0.7), 193 (M+1, 9.8), 192 (M, 78), 191 (BP, 100), 190 (6), 189 (32), 165 (19), 164 (4), 163 (5), 96 (9), 95 (10), 94 (16), 83 (5), 82 (12), 63 (3). UV (MeOH), λ<sub>max</sub> nm, lg ε<sub>max</sub>: 212 (4.37), 221 (4.35), 285.5 (4.09). Anal. calcd. for C<sub>15</sub>H<sub>12</sub> (192.26): C, 93.70; H, 6.29. Found: C, 93.65; H, 6.11%.

**5H-10,11-Dihydro-dibenzo[*a,d*]cyclohepten-5-one (dibenzosuberone) (4).** bp 193-194°C/3 mbar (lit.<sup>8</sup> bp 185-195°C/3 mbar; bp 135-140°C/0.05 mbar). <sup>1</sup>H-NMR (300 MHz): δ=8.00 (dd, 2H, H-4, H-6, J<sub>4(6), 3(7)</sub>=7.6 Hz, J<sub>4(6), 2(8)</sub>=1.4 Hz), δ=7.43 (dd, 2H, H-2, H-8, J<sub>2(8), 1(9)</sub>=7.6 Hz, J<sub>2(8), 4(6)</sub>=1.4 Hz), δ=7.32 (td, 2H, H-3, H-7, J<sub>3(7), 4(6)</sub>=7.6 Hz, J<sub>3(7), 1(9)</sub>=1.2 Hz), δ=7.20 (dd, 2H, H-1, H-9, J<sub>1(9), 2(8)</sub>=7.6 Hz, J<sub>1(9), 3(7)</sub>=1.2 Hz), δ=3.20 (s, 4H, 2H-10, 2H-11). <sup>13</sup>C-NMR: δ=195.63 (C-5), 141.92 (C-9a, C-11a), 138.58 (C-4a, C-5a), 132.34 (C-2, C-8), 130.53 (C-4, C-6), 129.25 (C-1, C-9), 126.59 (C-3, C-7), 34.92 (C-10, C-11). IR (CCl<sub>4</sub>), ν/cm<sup>-1</sup>: 3065, 3026, 2950, 2922, 2860, 1655 (C=O), 1600, 1450, 1295, 1250, 1221, 1150, 940. MS, m/e %: 210 (M+2, 7.5), 209 (M+1, 13), 208 (BP, M, 100), 207 (5), 193 (8), 181 (7), 180 (46), 179 (56), 178 (39), 176 (13), 166 (3), 165 (38), 152 (7), 151 (15), 139 (3), 115 (3), 103 (3), 102 (3), 90 (7), 89 (21), 77 (5), 76 (9), 63 (8), 51 (7), 50 (4). UV (MeOH), λ<sub>max</sub> nm, lg ε<sub>max</sub>: 208.5 (4.21), 228 sh (3.67), 270 (4.01). Anal. calcd. for C<sub>15</sub>H<sub>12</sub>O (208.26): C, 86.51; H, 5.81. Found: C, 86.34; H, 5.71%.

**5H-10,11-Dihydro-dibenzo[*a,d*]cycloheptene (1).** mp 133-134°C (lit.<sup>12</sup> mp 134°C). <sup>1</sup>H-NMR (300 MHz): δ=7.08-7.20 (m, 8H, H-1-4, H-6-9), 4.08 (s, 2H, H-5), 3.14 (s, 4H, H-10, H-11). <sup>13</sup>C-NMR: δ=139.24 (C-9a, C-11a), 138.95 (C-4a, C-5a), 129.52\* (C-4, C-6), 128.96\* (C-1, C-9), 126.56 (C-2, C-8), 126.01 (C-3, C-7), 40.98 (C-5), 32.50 (C-10, C-11). IR(KBr), ν/cm<sup>-1</sup>: 3060, 3026, 3009, 2932, 2913, 2877, 2834, 1573, 1491, 1445, 1358, 1293, 1101, 951, 910, 825, 760, 710, 697, 620. MS, m/e %: 196 (M+2, 0.3), 195 (M+1, 9.5), 194 (BP, M, 100), 193 (39), 189

\* The attributions may be interchanged.

(10), 180 (7), 179 (54), 178 (20), 177 (45), 176 (5), 165 (23), 152 (11), 128 (6), 117 (7), 116 (23), 115 (29), 96 (9), 94 (6), 91 (6), 90 (10), 89 (13), 83 (5), 82 (9), 77 (4), 76 (5), 63 (5). UV (MeOH),  $\lambda_{\max}$  nm, lg  $\epsilon_{\max}$ : 211 (4.37), 269.5 (2.78). Anal. calcd. for C<sub>15</sub>H<sub>14</sub> (194.27): C, 92.73; H, 7.26. Found: C, 92.68; H, 7.11%.

**5-Methylene-5H-dibenzo[*a,d*]cycloheptene (11).** mp 119 (lit.<sup>13</sup> mp 119-119.6°C). <sup>1</sup>H-NMR (300 MHz):  $\delta$ =7.25-7.42 (m, 8H, H-1-4, H-6-9), 6.83 (s, 2H, H-10, H-11), 5.26 (s, 2H, H-12). <sup>13</sup>C-NMR:  $\delta$ =150.94 (C-5), 140.91 (C-9a, C-11a), 134.00 (C-4a, C-5a), 131.26 (C-10, C-11), 128.77 (C-4, C-6), 128.63 (C-1, C-9), 128.02 (C-2, C-8), 127.40 (C-3, C-7), 120.35 (C-12). IR (KBr),  $\nu/\text{cm}^{-1}$ : 3091, 3060, 3022, 1612 (C=C), 1593, 1553, 1481, 1431, 1314, 1157, 1037, 968, 951, 907, 814, 800, 777, 716. MS, m/e %: 206 (M+2, 0.5), 205 (M+1, 13), 204 (BP, M, 100), 203 (82), 202 (50), 200 (18), 189 (7), 178 (3), 176 (8), 163 (4), 152 (4), 151 (3), 150 (5), 102 (5), 101 (16), 100 (18), 99 (3), 89 (8), 88 (10), 76 (4), 63 (4), 51 (3), 50 (3). UV (MeOH),  $\lambda_{\max}$  nm, lg  $\epsilon_{\max}$ : 227 (4.56), 245sh (4.28), 295 (3.98). Anal. calcd. for C<sub>16</sub>H<sub>12</sub> (204.27): C, 94.08; H, 5.92. Found: C, 94.00; H, 5.76%.

## References

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