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Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)

FLOW-VACUUM PYROLYSIS OF POLYCYCLIC COMPOUNDS. 24.[1] PYROLYSIS OF TWO DIBENZOCYCLOALKANOLS AND THEIR CORRESPONDING ACETATES

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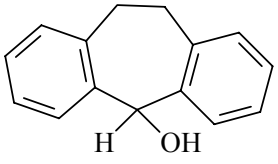
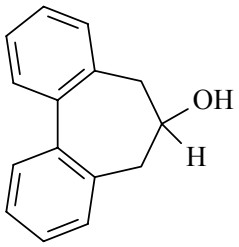
The flow-vacuum pyrolyses of 6-hydroxymethyl-6H-5,7-dihydrodibenzo[*a,c*]cycloheptene (**4**), 6-methyl-6H-5,7-dihydro-dibenzo[*a,c*]cyclohepten-6-ol (**5**) and their corresponding acetates (**6**) and (**7**) were studied. The products' distributions were determined by GC/MS and the reaction mechanisms involving radical species were suggested, in order to explain the formation of the main reaction products.

INTRODUCTION

In our previous papers we described the thermal behaviour in flow-vacuum pyrolysis (FVP) of the dibenzocycloalkanols[2-5] such as: **1**[3] and **2**[4] with dibenzocycloheptene skeleton:



1



2

In FVP conditions[6] we observed rearrangements and aromatization processes, the main products being anthracene, respectively phenantrene derivatives. Formation of all reaction products was explained through radical mechanisms.

In order to obtain new evidence concerning the reaction mechanisms for dibenzocycloheptane derivatives, we present herein the thermal behaviour of 6-hydroxymethyl-6H-5,7-dihydrodibenzo[*a,c*] cycloheptene(**4**), 6-methyl-6H-5,7-dihydrodibenzo[*a,c*]cyclohepten-6-ol (**5**) and their corresponding acetates (**6**) and (**7**):

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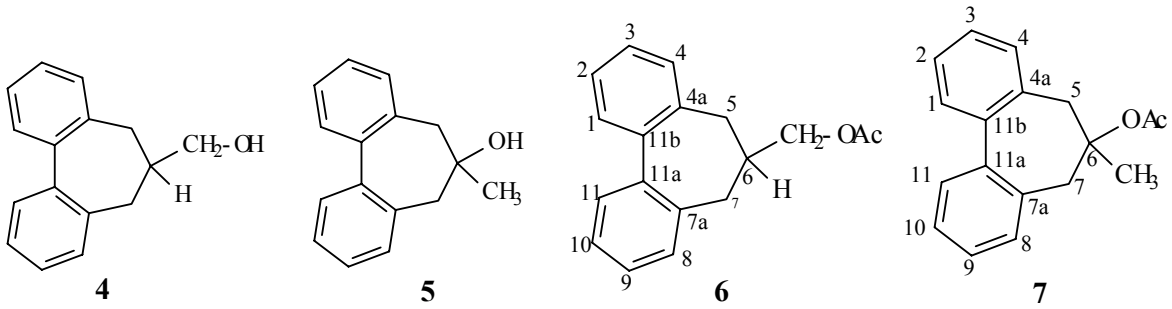


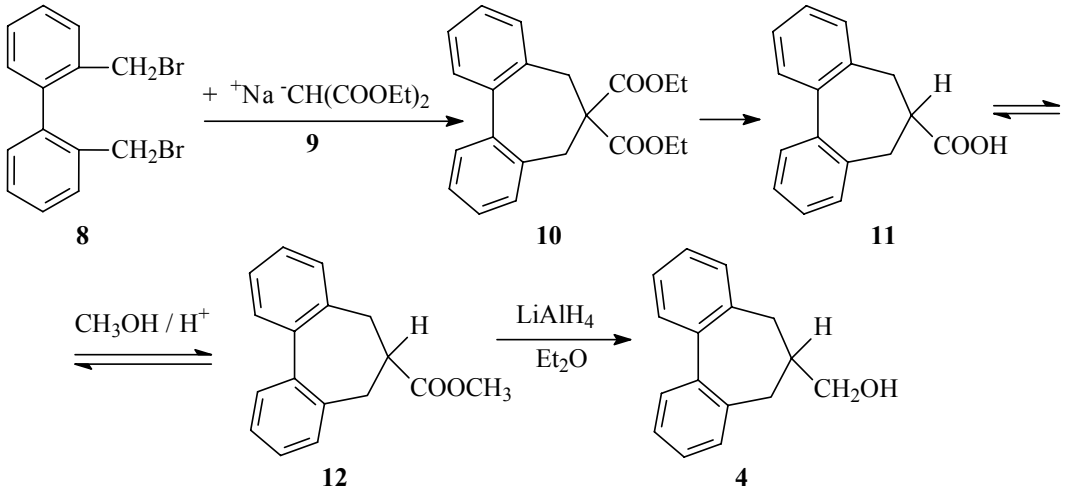
4 **5** **6** **7**

The scarcity of literature information about thermal behaviour of the acetates with dibenzocycloalcane skeleton[7] was another reason for starting our study.

RESULTS

Syntheses

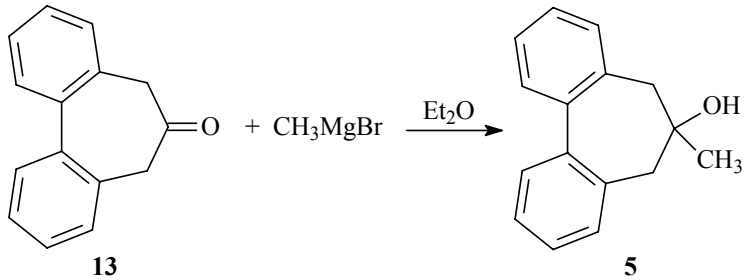
The synthesis of alcohol **4** was performed following literature data[8] (**Scheme 1**):



8 **10** **11** **12** **4**

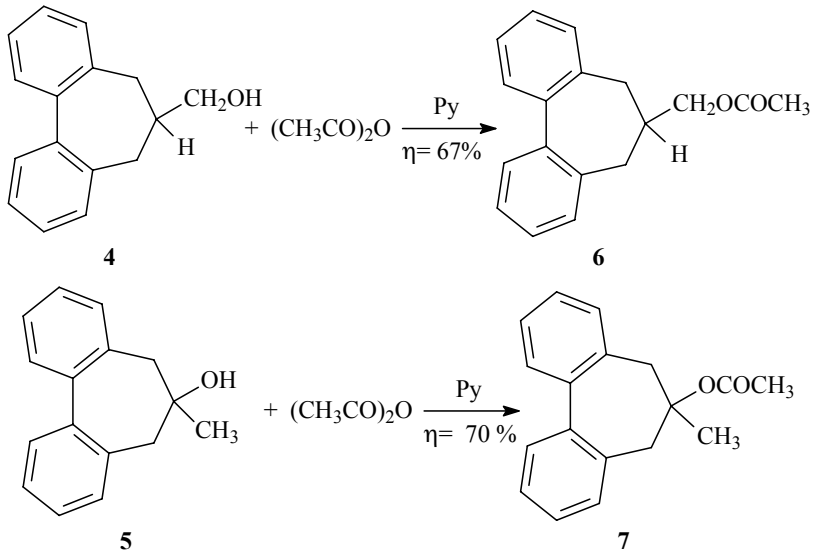
Scheme 1

The alcohol **5** was obtained from the corresponding ketone **13** with methylmagnesium bromide[9]:



13 **5**

The acetates **6** and **7** were prepared from the corresponding alcohols **4** and respectively **5**, with acetic anhydride in pyridine, at room temperature (*see* Experimental Part):



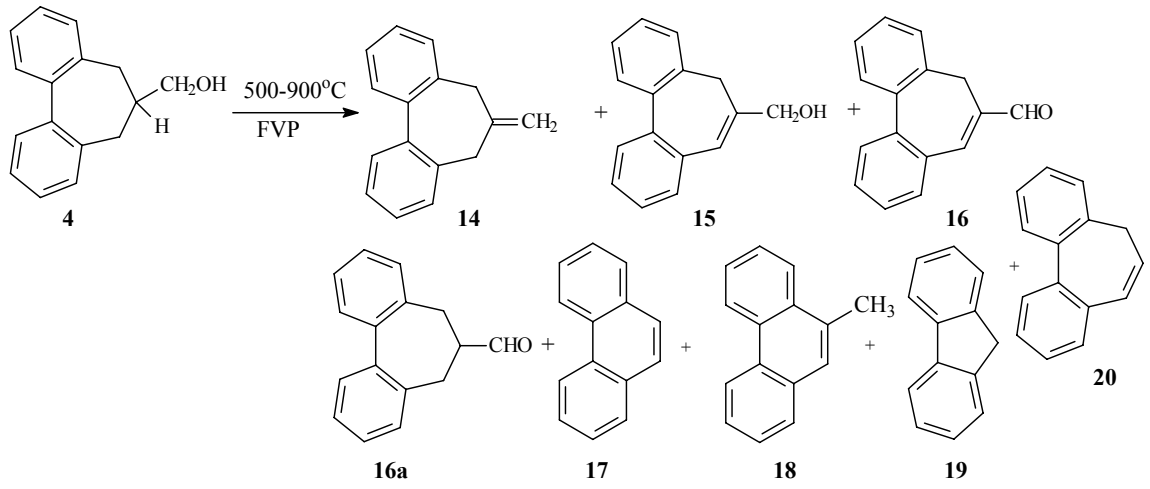
Pyrolyses

General procedure

For a good correlation of experimental data between the previous and present results we performed the flow-vacuum pyrolyses of dibenzocycloheptane derivatives **4 – 7** in the same described conditions[6]: the pyrolysis quartz tube (60 cm length, 10 mm internal diameter) was filled with quartz chips on 30 cm length; this zone was heated with a cylindrical electric oven. The temperature was continuously measured by a thermocouple and the pressure (~1 mmHg) with a McLeod manometer. The sample (usually ~ 30 mg) was sublimed under argon flow (4 ml/min) in the pyrolysis tube. The reaction products were dissolved in dichloromethane, the solvent was evaporated *in vacuum* and the residue was analysed by GC/MS (*see* Experimental). Analytical pyrolyses at optimal temperature were followed by preparative runs in order to isolate the main products or for spectra registration.

Pyrolysis of 6-hydroxymethyl-6*H*-5,7-dihydro-dibenzo[*a,c*]cycloheptene (4)

This compound is very stable: at 550°C was converted ~ 1% and only at 900°C was completely transformed. The main products (of the very complex mixture) resulted in this pyrolysis are presented in **Scheme 2** and **Table 1:**



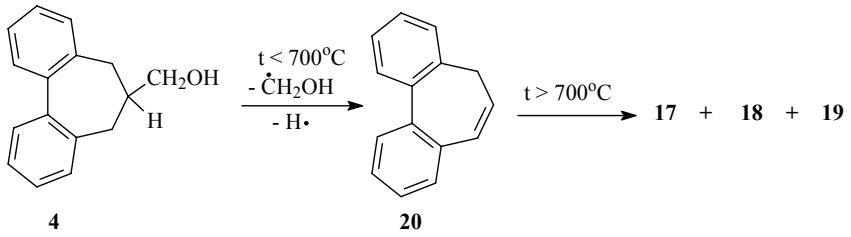
Scheme 2

Table 1

Product' distribution in pyrolyses of **4**

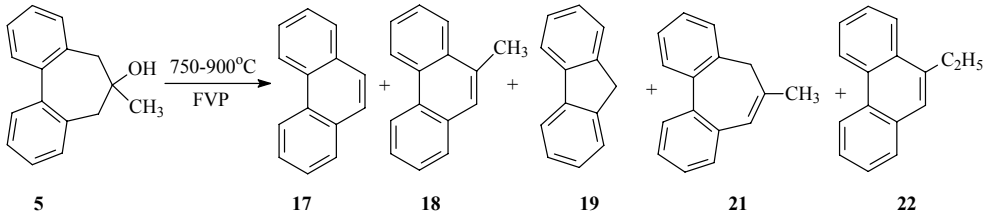
Compound	Pyrolysis products of 7 at different temperatures (%)						
	550°C	**600°C**	**700°C**	**750°C**	**800°C**	**850°C**	**900°C**
14	0	0	0	3	3	4	10
15	0	0	0	2	2	9	13
16	0	0	2.4	4	5	6	13
16a	0	0	0	0	2	37	3
17	0	0	1	1.5	2	3	19
18	0	0	0	2	5	5.5	31
19	0.6	2.5	0	0	0	0	0
20	3	4	3	0	0	0	0
4 (unreacted)	96	93	90	87	79	38	10

The last compounds (**17**–**19**) were formed by decomposition of 5*H*-diben-zo[*a,c*]cycloheptene (**20**), instable over 700°C[10]:



Pyrolysis of 6-methyl-5,7-dihydrodibenzo[*a,c*]cycloheptene-6-ol (5)

The alcohol **5** was pyrolysed between 750°C – 900°C and the products' distribution is presented in **Scheme 3**; their distribution at different temperatures is displayed in **Fig. 1**:



Scheme 3

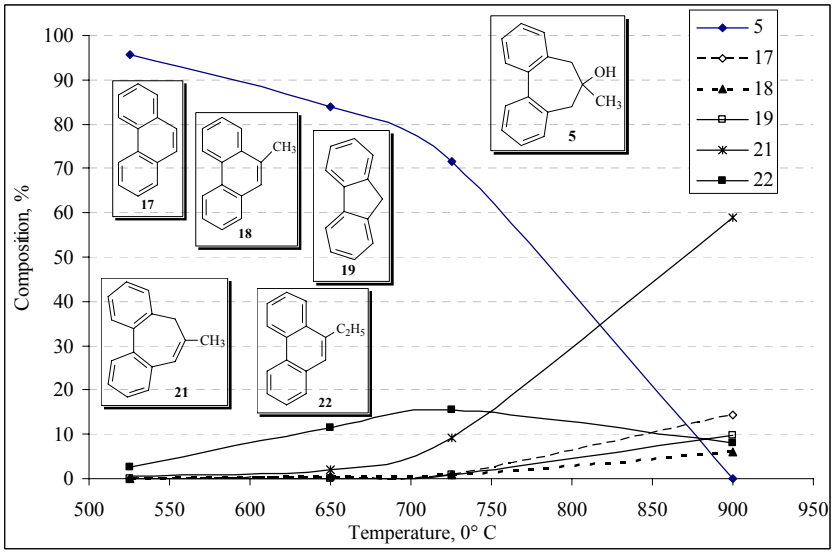
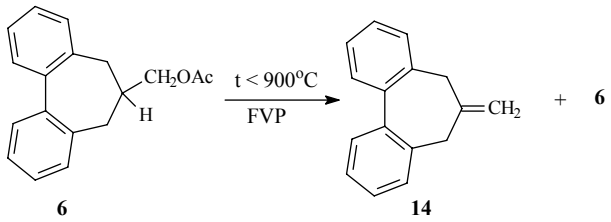


Fig. 1 – Main pyrolysis products' distribution of acetate **5** related to temperature.

Pyrolysis of acetate 6

The acetate **6** proved to be a very stable compound: at 800°C it was transformed 7% and at 900°C ~ 65%. The main pyrolysis product is the *exo*-cyclic alkene **14** (**Scheme 4**) and the distribution at different temperatures is displayed in **Fig. 2**:



Scheme 4

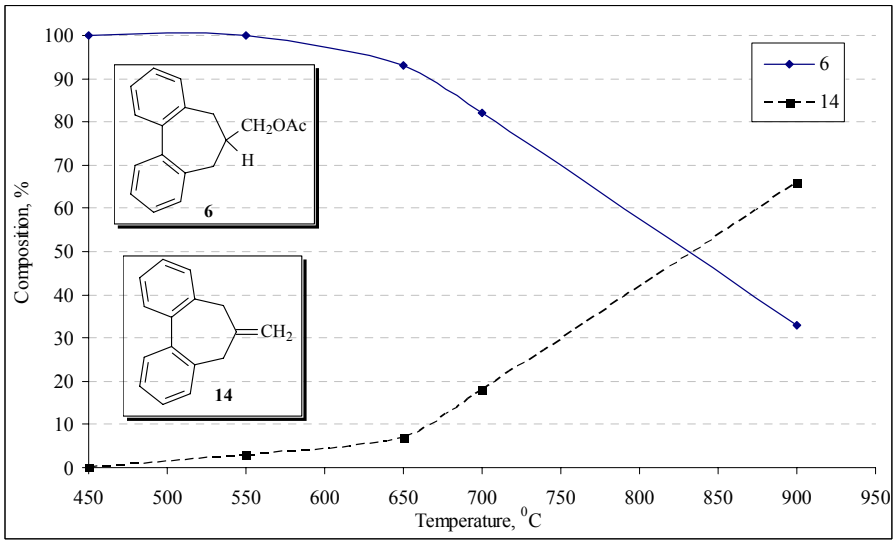
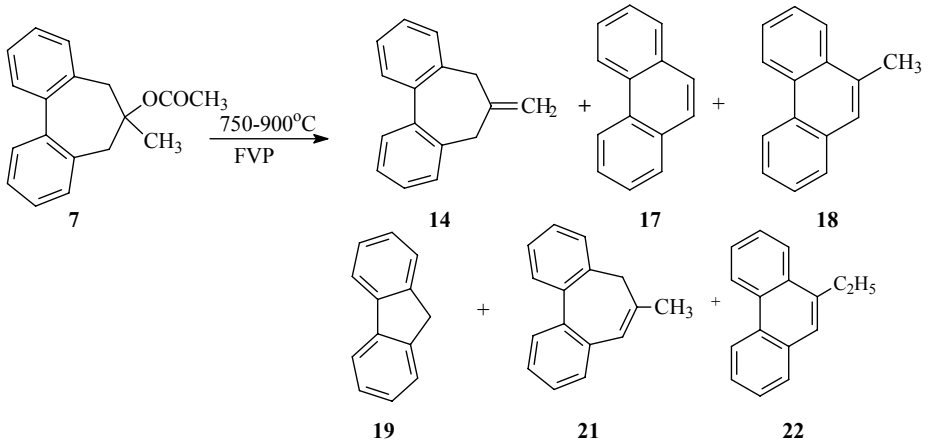


Fig. 2 – Pyrolysis product's distribution of acetate **6** related to temperature.

Pyrolysis of acetate 7

The isomer acetate **7** showed a different stability: at 650°C it was completely transformed and the main products were: the *intra*-cyclic alkene **21** (79%) and its *exo*-cyclic isomer, the alkene **14** (~10%). At 900°C the products distribution is more complex because the alkenes **14** and **21** were partially converted in more stable compounds. The products of the pyrolysis are presented in **Scheme 5** and in **Table 1**:



Scheme 5

Table 2

Products' distribution in pyrolyses of **7**

Compound	Pyrolysis products of 7 at different temperatures (%)		
	650°C	**800°C**	**900°C**
14	10.4	11.0	10.0
17	0	0	0.9
18	0	0	0.5
19	0	0	0.2
21	79.3	73.6	72.4
22	0	0	2.2
5	0	0	2.2
7 (unreacted)	0	0	0

DISCUSSION

The mechanism for pyrolysis of 6-hydroxymethyl-6H-5,7-dihydrodibenzo-[*a,c*]cycloheptene (**4**), suggesting the rationalization of reaction products' occurrence, is presented in **Scheme 6**.

The break of radical $^{\cdot}CH_2OH$ needs about 84 kcal/mol[11] and generates the radical **4a** which is easily converted into dibenzocycloalkene **20**. At higher temperature (over 700°C) this alkene is converted into aromatic hydrocarbons[9]: methyl-phenanthrene and phenanthrene. On the other route **b)**, the extraction of secondary hydrogen atom needs about 85 kcal/mol[11] and the radical **4b** is formed; the hydrogen atom elimination generates the unsaturated alcohol **15**.

The unsaturated aldehyde **16** may be formed by route **c)**: the elimination of a hydrogen atom generates the radical **4c**, easily converted into unstable saturated aldehyde **16A** (M=222). This is finally transformed into aldehyde **16** (M=220).

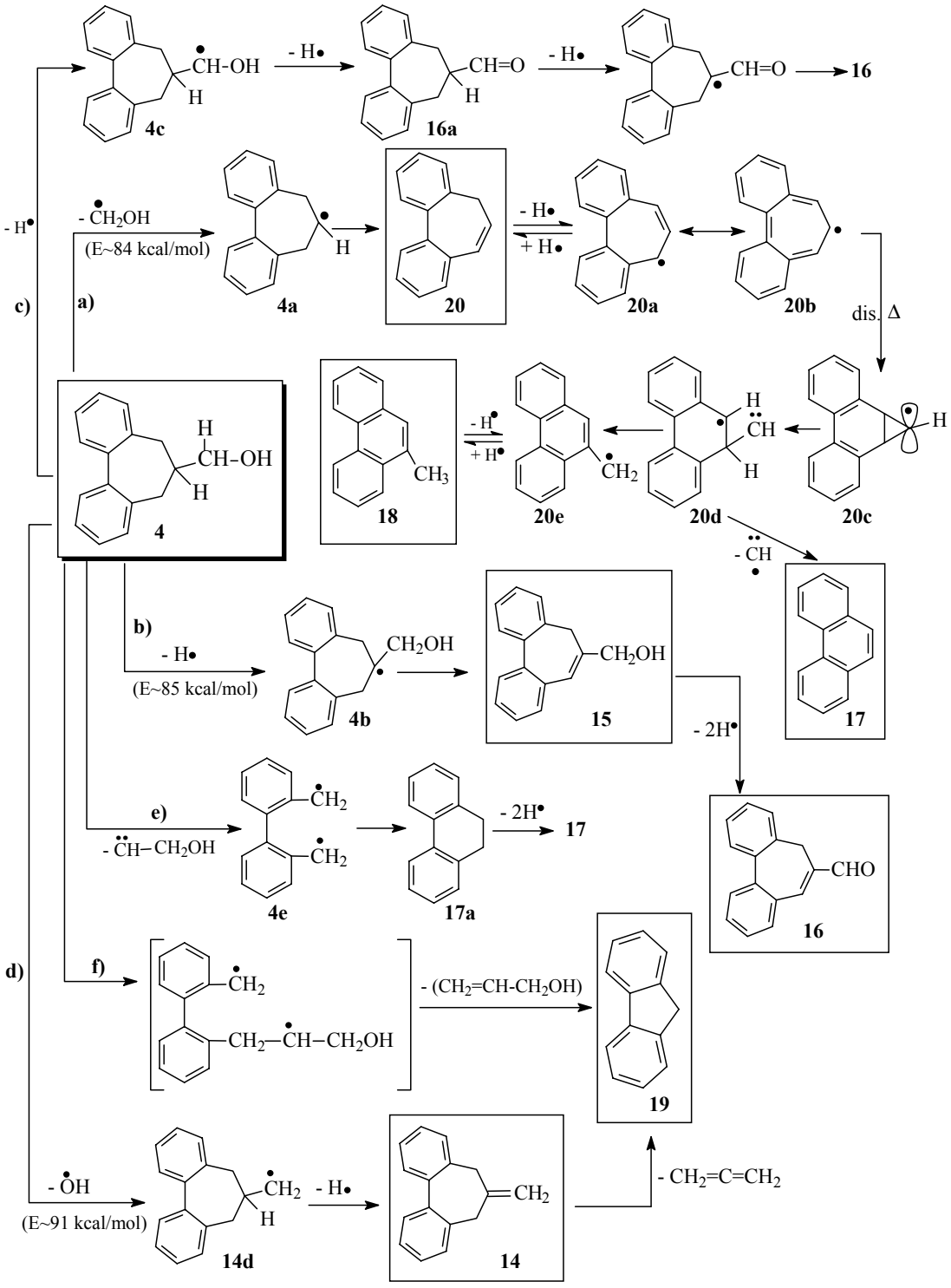
Break of a radical hydroxyl ($^{\cdot}OH$) needs about 91 kcal/mol[11] for generating the very unstable (primary) radical **4d**; this one is easily stabilised by hydrogen-atom elimination, when the methylenedibenzocycloheptene (**14**, M=206) is formed. Acetaldehyde elimination [route **e)**] generates the benzyl diradical **4e**; the phenanthrene (**17**, M=178) is produced by cyclization, followed by the aromatization[12] of dihydrophenanthrene (**17A**, M=180). The presence of small amount of fluorene (**19**, M=166) can be explained by a radical break **f)** of **4**, followed by a loss of undetected allylic alcohol, accompanied by cyclization.

The thermal behaviour of the secondary alcohol 6-methyl-6H-5,7-dihydrodiben-zo[*a,c*]cyclohepten-6-ol (**5**) was studied between 650 – 900°C and the products' distribution is rationalized in **Scheme 7**.

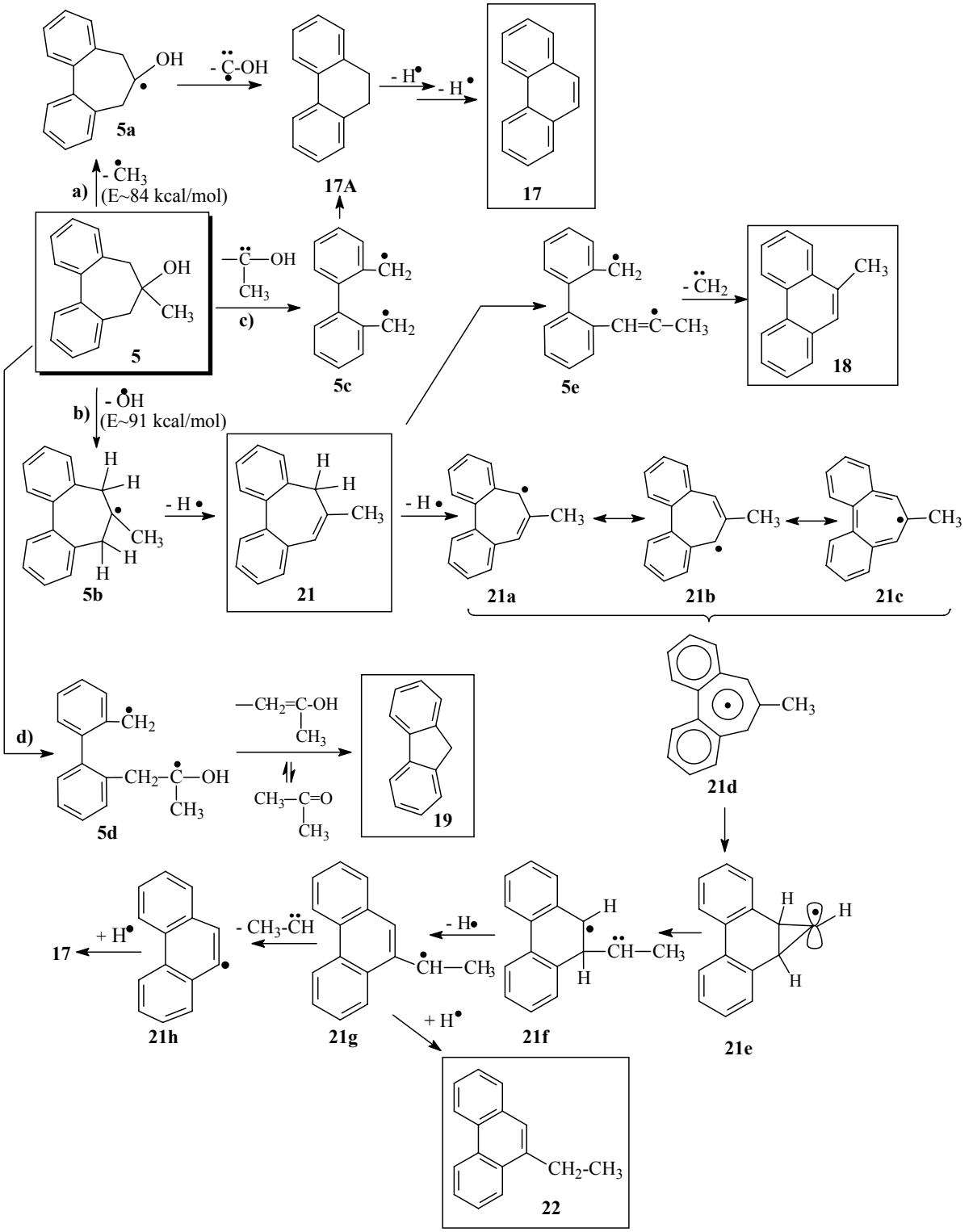
The methyl radical break needs about 84 kcal/mol[11] and generates the secondary radical **5a** which is converted into dihydrophenantrene (**17A**)**.** By a subsequent aromatization the phenanthrene (**17**) is formed. The route **b)** (break of hydroxyl radical $^{\cdot}OH$) needs larger dissociation energy than route **a)** (*see* **Scheme 7**). The radical **5b** is stabilised with formation of alkene **21** as major product. This compound is converted over 750°C into more stable products: fluorene (**19**), phenanthrene (**17**) and ethyl-phenanthrene (**22**).

The route **c)** indicates the elimination of acetaldehyde with generation of stable dibenzylic diradical **5c**, which is stabilized with formation of dihydrophenanthrene (**17A**). Phenanthrene (**17**) is then formed by aromatization. Formation of fluorene is rationalized also by route **d)**: the break of the C-C bond with generation of diradical **5d**, stabilised by acetone elimination.

Formation of 9-methyl-phenantrene (**18**) is explained by generation of diradical **5e** which is stabilized by methylene carbene elimination.

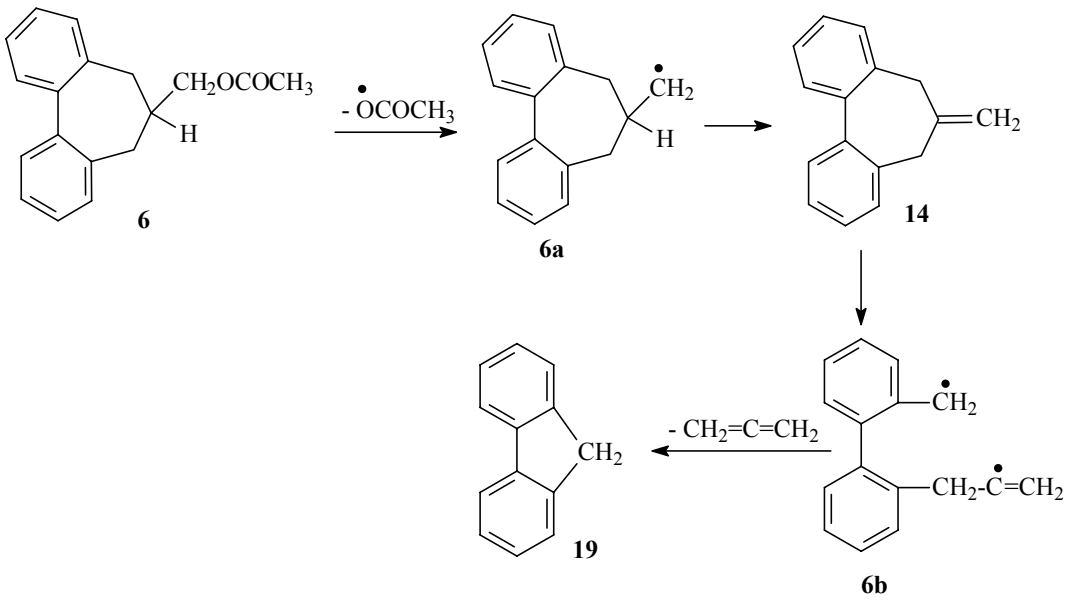

- H•
c)
a)
- •CH2OH
(E~84 kcal/mol)
4a
20
- H•
+ H•
20a
20b
dis. Δ
4
18
- H•
+ H•
20e
20d
20c
- :CH•
17
b)
- H•
(E~85 kcal/mol)
4b
15
- 2H•
16
e)
- :CH–CH2OH
4e
17a
- 2H•
17
d)
f)
- (CH2=CH-CH2OH)
19
- •OH
(E~91 kcal/mol)
14d
- H•
14
- CH2=C=CH2
4c
- H•
16a
- H•
16

Scheme 6



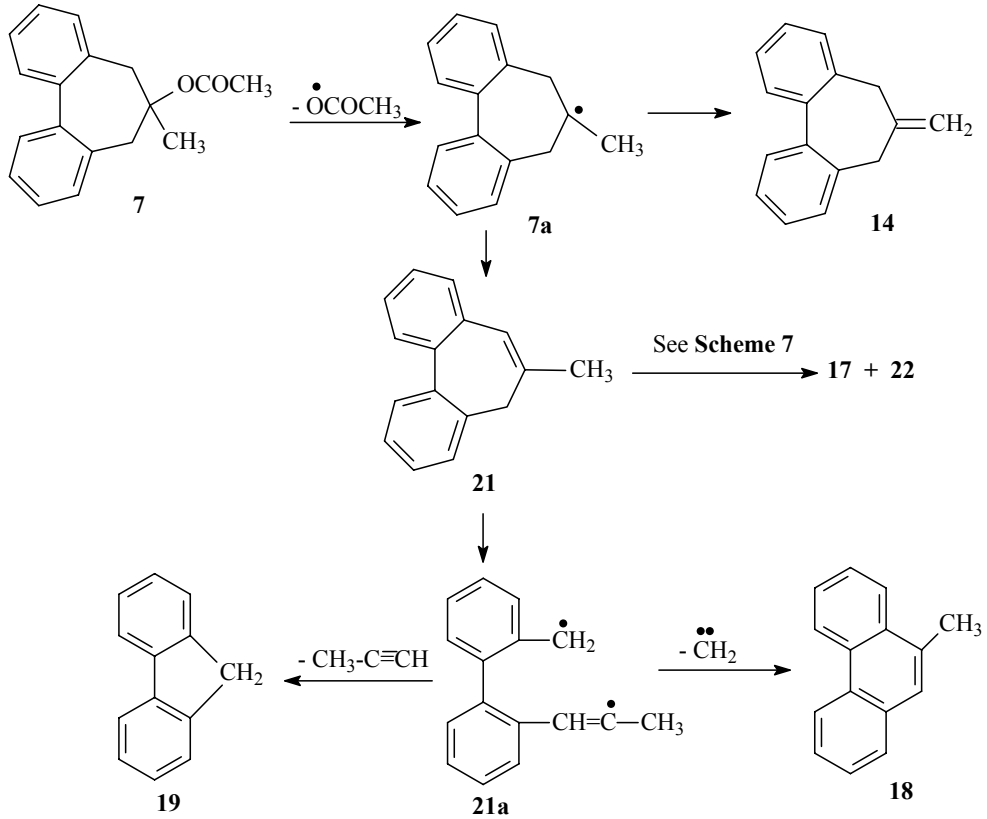
Scheme 7

The rationalization of the thermal behaviour of the acetate **6** in flow-vacuum pyrolysis is presented in **Scheme 8**:



Scheme 8

The break of ·$OCOCH_3$ fragment generates the unstable primary radical **6a** which is converted into alkene **14** by the ·H elimination. At higher temperature, this alkene is partially transformed into small amounts of fluorene (**19**): the break of the C-C bond generates the diradical **6b**, which is stabilized with formation of fluorene by alene elimination.



Scheme 9

The mechanism suggested for pyrolysis of the acetate **7** (isomer of acetate **6**) is presented in **Scheme 9**.

The tertiary radical **7a** is formed by breaking of $^{\cdot}OCOCH_3$ and can be stabilized with the generation of two alkenes **21** (major product) and **14** (minor product). At 650°C the main pyrolysis product, alkene **21**, represents 79.3% and at 900°, 72.4%. The small amounts of stable aromatic products (fluorene, phenanthrene and ethyl-phenanthrene) were explained by thermal decomposition of the alkenes **21** (*see* **Scheme 7**) and **14** (*see* **Scheme 8**).

CONCLUSIONS

The hereby presented work focused on:

The synthesis and spectral characterization of two isomeric acetates (**6** and **7**) with dibenzocycloheptenic skeleton.

The flow-vacuum pyrolysis of two isomeric alcohols (**4**, **5**) and their corresponding acetates (**6**, **7**). The products' distribution of each starting compound was discussed and radicalic mechanisms of conversion were proposed.

The pyrolysis of primary and secondary dibenzo[*a,d*]cycloheptenic alcohols **4** and **5** resembles with that of the saturated derivatives, previously investigated in our group.[3]

The pyrolysis of the two acetates (**6**, **7**) with dibenzocycloheptenic skeleton confirmed the previous results[7] involving acetic acid elimination. At higher temperature the more stable compounds, alkene **14** and **21** respectively, were formed.

The mechanisms previously suggested involved the radicals' generation, which leading final stable compounds, especially aromatized hydrocarbons.

EXPERIMENTAL PART

Apparatus for physical analyses

Melting points are uncorrected. IR spectra were registered on a Bruker Equinox 55 spectrometer. The NMR spectra were registered at 300 MHz (^{1}H-) and 75 MHz (^{13}C) on a Varian Gemini 300 apparatus using TMS as internal standard. The GC/MS analyses for pyrolyses of compounds **4** and **6** 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 length, 0.25 mm internal diameter) was used. The analysis conditions were: injector temperature: 250°C; split rate 1:50; temperature program: 50 – 250°C at 5°C/min and then 20 min. at 250°C; carrier gas: helium (flow-rate of 1 mL/min); temperature of transfer line: 275°C; trap temperature: 170°C; electron ionisation: 70 eV. The GC/MS analyses for pyrolyses of compounds **5** and **7** were performed on an Agilent GC/MS with split/splitless injector, quadrupole, a capillary DB-5-MS (25 m length, 0.25 mm internal diameter, carrier gas: helium (flow-rate of 0.5 mL/min); temperature program: 50°C – 100°C at 5°C/min, 100°C - 280°C at 10°C/min and then 15 min. at 280°C; electron ionisation: 70 eV.

The GC/MS analyses for pyrolyses of compounds **5** and **7** were performed on an Agilent GC/MS with split/splitless injector, a capillary DB-5 MS (25 m length, 0.25 mm internal diameter), carrier gas: helium (flow rate of 0.5 mL/min); temperature program: 50 – 100°C at 5°C/min, 100-280°C at 10°C/min and then 15 min at 280°C.

Synthesis of acetate 6

1 g (4.4 mmol) of alcohol **4** with 10 mL pyridine was cooled at 0°C under magnetically stirring. 3 mL of acetic anhydride were added and the reaction mixture was stirred for 6 hours at 50°C and the solvent was *vacuum* evaporated. The residue was extracted with chloroform (3 x 20 mL) and the chloroform layers were washed with 10% hydrochloric acid solution and with water until pH = 7. The solvent was evaporated and the yellow-brown solid (η = 67%) was recrystallized (m.p. = 53°C, methanol) and analysed:

IR spectrum (KBr, ν, cm^{-1}): 750vs; 1035vs; 1228vs; 1366s; 1453s; 1481s; 1739vs ($\nu_{C=O}$); 2854s; 2942vs; 3016m; 3063m.

^{1}H-NMR spectrum ($CDCl_3$, δ, ppm): 2.09 (s, 3H, CH_3); 2.6 (dd, 4H, $H^{5,7}$); 2.71 (q, 1H, H^6); 4.03 (d, 2H, CH_2-O); 7.2 (m, 2Harom., $H^{4,8}$); 7.3 (m, 2Harom., $H^{3,9}$); 7.35 (m, 2Harom., $H^{2,10}$); 7.5 (m, 2Harom., $H^{1,11}$).

^{13}C- NMR spectrum ($CDCl_3$, δ, ppm): 20.99 (CH_3); 33.82 (C^5 C^7); 43.82 (C^6); 66.52 (CH_2-O); 127.02 (C^3, C^9); 127.47 (C^4,C^8); 128.26 (C^2, C^{10}); 129.21 (C^1, C^{11}); 129.25 (2Cq, $C^{11a,11b}$); 140.81 (2Cq, $C^{4a,7a}$); 171.12 (C=O).

MS spectrum (m/e, relative abundance %): 43 (16); 115 (5); 152 (8); 165 (38); 166 (9); 176 (5); 177 (5); 178 (75); 179 (24); 188 (12); 189 (12); 190 (9); 191 (B.P., 100); 192 (20); 193 (8); 203 (5); 205 (36); 206 (82); 207 (15); 266 (M, 25); 267 (M+1,5).

Synthesis of acetate 7

2g (7.5 mmol) of alcohol **5** in 15 mL pyridine at 0°C were treated with 5 mL of acetic anhydride, under magnetic stirring. The reaction mixture was maintained 24 hours at 50°C. After *vacuum* evaporation of pyridine, 20 mL 5% HCl solution were added. The mixture was extracted with chloroform (3x20 mL). The organic layers were washed with 5% HCl solution (in order to eliminate traces of pyridine) and then with water (until neutral). A mixture of acetate **7** and starting alcohol **5** was obtained after solvent evaporation. Acetate **7** was separated by liquid chromatography (SiO_2, benzene as eluent) as a viscous yellow liquid (η = 70%).

IR spectrum ($CHCl_3$, ν, cm^{-1}): 750vs, 906vs, 1125vs, 1370m, 1453vs, 1480vs, 2966m.

^{1}H-NMR spectrum ($CDCl_3$, δ, ppm):CD_3NO_2, δ, ppm, J, Hz): 1.64 (s, 3H, CH_3); 1.97 (s, 3H, $COCH_3$); 2.20 – 3.60* (sl, 4H, $2H^5$, $2H^7$); 7.28 (dd, 7.4; 1.7; 2H, $H^{3,9}$); 7.32 (td, 7.4; 1.7; 2H, $H^{2,10}$); 7.40 (td 7.4;1.7; 2H $H^{1,8}$); 7.48 (dd, 7.4; 1.7; 2H, $H^{1,11}$).

* The benzylic protons' system ($H^{5,7}$) is a large singlet at room temperature. In CD_3NO_2 at 90°C it becomes an AB system with J=13.5 Hz at δ = 2.76 and δ = 2.93 respectively.

^{13}C- NMR spectrum ($CDCl_3$, δ, ppm): 22.31 (CH_3); 23.36 ($\mathbf{C}H_3CO$); 91.05 (C^6); 43.09 ; 43.40 (C^5, C^6); 127.19 (CH); 127.31 (CH); 128.05 (CH); 129.51 (CH); 140.51(C^{4a}, C^{7a}); 136.28(C^{11a}, C^{11b}); 170.50 (C=O).

MS spectrum (m/e, relative abundance %): 43 (21); 89 (7); 152 (7); 165 (30); 166 (13); 176 (5); 178 (23); 179 (16); 181 (13); 189 (14); 190 (10); 191 (B.P., 100); 192 (19); 205 (9); 206 (95); 207 (20).

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