THERMAL DECOMPOSITION OF POLYCYCLIC ACETATES OVER HZSM-5 ZEOLITE IN FLOW-VACUUM CONDITIONS

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The thermal decomposition of the 10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-acetate (**7**), 5*H*-6,7-dihydrodibenzo[*a,c*]-cyclohepten-6-acetate (**8**) and 6-hydroxymethyl-*6H*-5,7-dihydrodibenzo[*a,c*]cycloheptene's acetate (**9**) in flow-vacuum conditions: advanced vaccum (0,1–0,2 Torr), inert atmosphere (argon), 250-350 ºC, over HZSM-5 zeolite was studyed. The products' distributions were determined by GC/MS using authentic samples. In order to explain the formation of the main reaction products, reaction mechanisms involving carbenium ions were suggested. A comparison between the thermal behaviour of polycyclic acetates **7-9** in flow-vacuum conditions over zeolite and quartz as catalyst was disscused.

INTRODUCTION

The flow-vacuum pyrolysis of dibenzocycloalkane skeleton systems (alcohols,[1] acetates[2]) represents an important domain for our research group owning to the possibility to highlight and/or to isolate some intermediates which can give information related to the radical reaction mechanism. These studies reveal systems' transposition during the thermal decomposition and aromatic stable derivatives are the main isolated products.

The flow-vacuum pyrolyses over zeolites of these systems bring an important change in thermal decomposition mechanism type: the used catalyst on a way and the thermal range on the other way (temperature under 350º C) imply ionic intermediates.

Banciu and coworkers[3,4] were the first researchers which address flow-vacuum thermal decompositions

over zeolites of the dibenzocycloalkane systems. There were studied the thermal behaviour of dibenzocycloalkane alcohols **1, 2** and their related acetates **3, 4** in flow-vacuum pyrolysis (FVP), over acid zeolites as catalyst.

1 (X: OH)
**3** (X: OCOCH₃)

2 (X: OH)
4 (X: OCOCH₃)
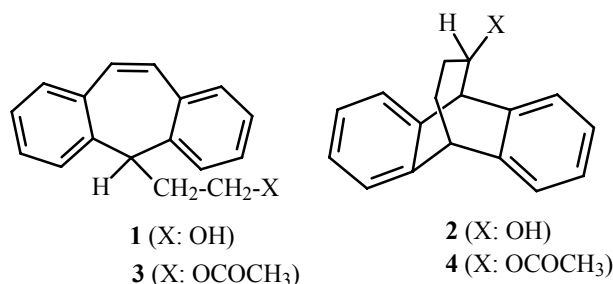
The thermal decomposition in flow-vacuum conditions over HZSM-5 and *β*-mesoporous zeolites as catalyst of dibenzo[*a,d*]cycloheptatrien-5-ol (**6**) was studied recently. [5]

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5   **6**
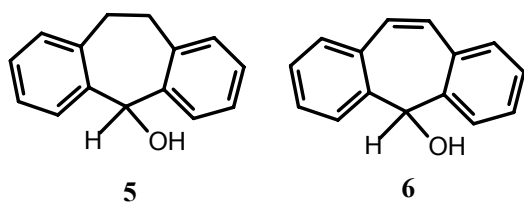
In order to obtain new data concerning the mechanisms of thermal decomposition reactions in flow-vacuum conditions (advanced vacuum, inert atmosphere) over zeolites of dibenzocycloalkane skeleton systems, the thermal behaviour of three dibenzoannelated acetates, 10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-acetate (**7**), 5*H*-6,7-dihydrodibenzo[*a,c*]-cyclohepten-6-acetate (**8**) and 6-hydroxymethyl-*6H*-5,7-dihydro-dibenzo[*a,c*]cyclo-heptene acetate (**9**), over HZSM-5 zeolite, at 250-350°C, was studied.


7   **8**   **9**
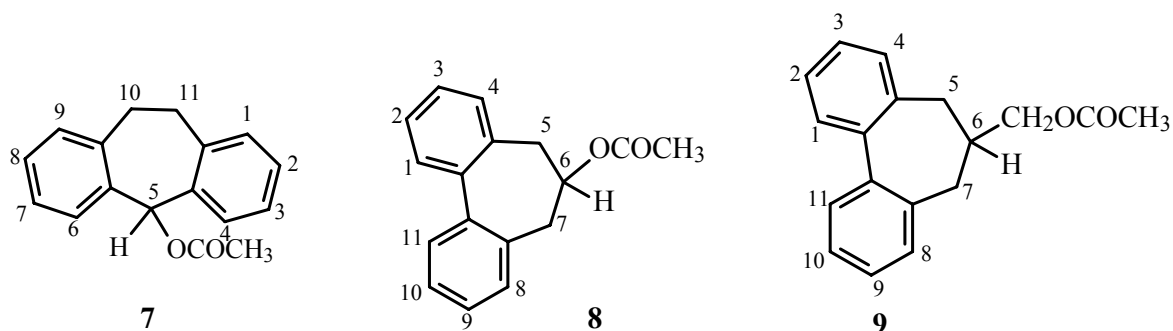
RESULTS AND DISCUSSION

1. Synthesis of acetates 7-9

Using literature data,[6] the syntheses of acetates **7-9** were performed starting from the corresponding dibenzocycloalkanols **10-12** and acetic anhydride in anhydrous pyridine, for 6-24 hours at 50°C (*see* Scheme 1). The obtained acetates were purified by liquid chromatography, and characterized by IR, ^{1}H- and ^{13}C-NMR.
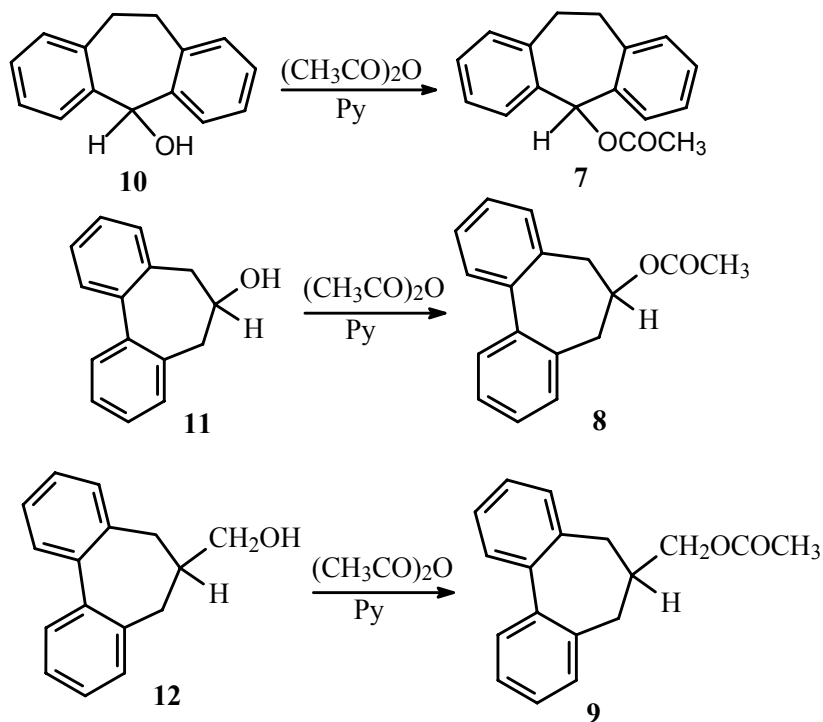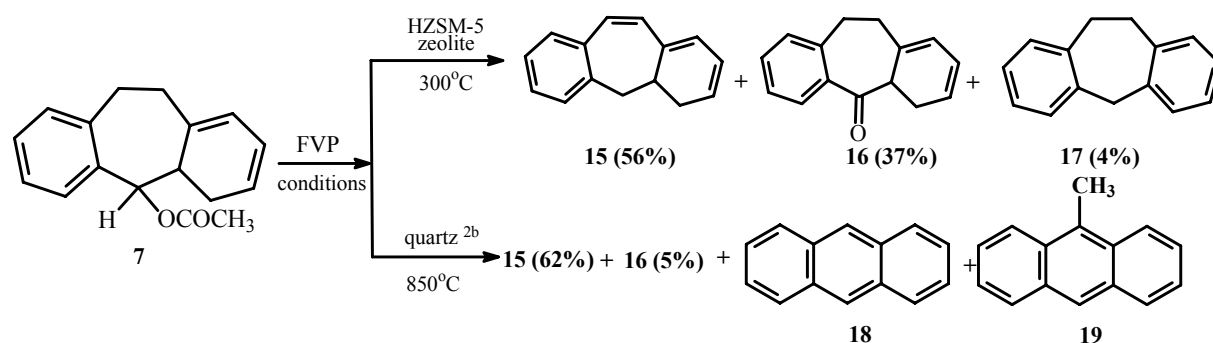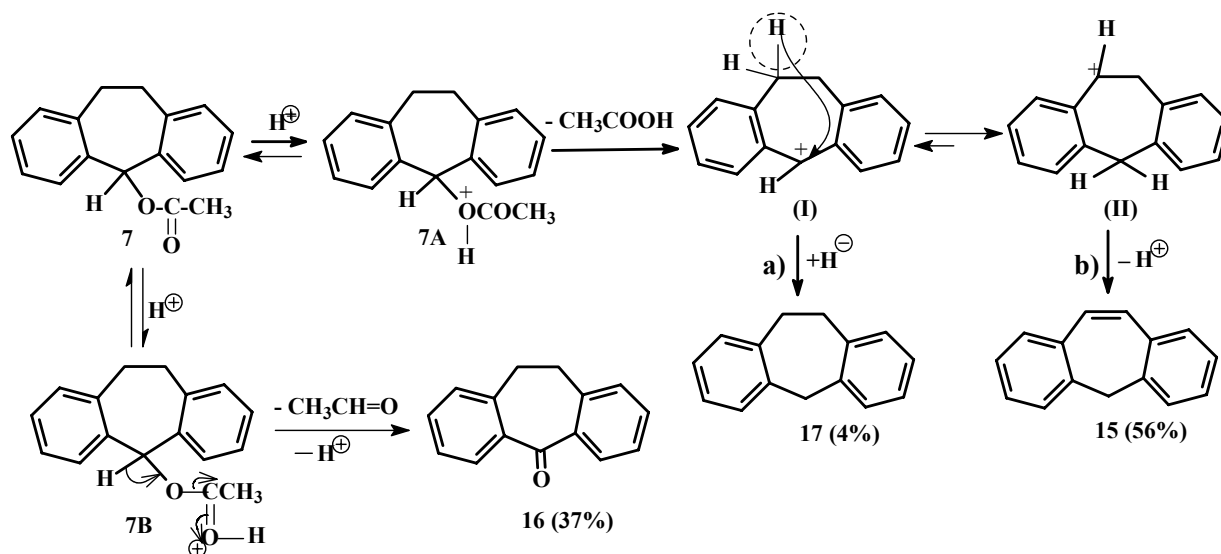

Scheme 1

2. Pyrolyses of acetates 7-9

2.1. Pyrolysis of 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-acetate (7)

The alkene **15**, the ketone **16** and the saturated hydrocarbon **17** are the products resulted from the FVP over HZSM-5 zeolite at 300°C of acetate **7** (*see* Scheme 2).

The proposed ionic mechanism for thermal decomposition of 10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-acetate (**7**) is presented in

Scheme 3. There are two possible reaction pathways with formation of **7A** and **7B** cations. In order to obtain more informations related to the proposed cationic intermediates, the MNDO semi-empiric calculations[7] for the corresponding alcohol were run and presented in a previously work.[5] The elimination of acetic acid molecule from cation **7A** affords two benzyl cations: (I) and (II), as precursors for formation of the dibenzocycloheptadiene (**15**) as main product and dibenzocycloheptane (**17**) as a minor product.
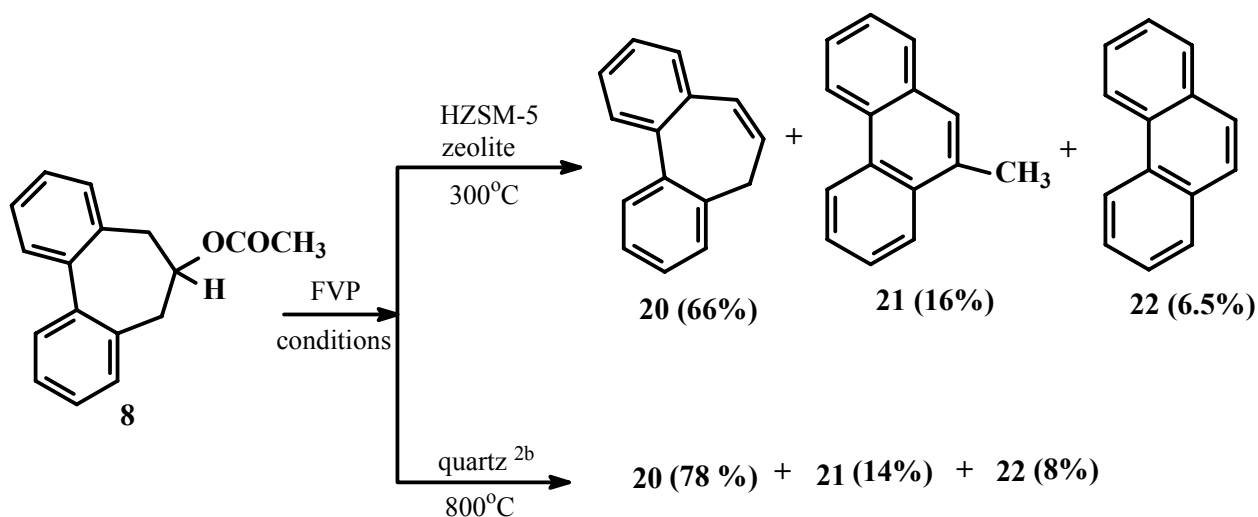

Scheme 2

Scheme 3

In the second pathway, the dibenzosuberone (**16**, 37%) was formed by acetaldehyde elimination.

A different products distribution was obtained in FVP over quartz of the same acetate. The presence of the anthracene (**18**) and the 9-methylanthracene (**19**) in the reaction mixture in this case can be explained by the alkene **15** transformation which is allowed only in the radicalic conditions (higher temperatures: 400-850°C)[2b] (*see* Scheme 2).

2.2. Pyrolysis of 5H-6,7-dihydrodibenzo[a,c]cyclohepten-6-acetate (8)

The reaction mixture obtained in the pyrolysis over HZSM-5 zeolite at 300°C of the acetate **8** contains the alkene **20** as major product, 9-methylphenanthrene (**21**) and phenanthrene (**22**) (*see* Scheme 4).

Scheme 4

In order to rationalize the products distribution an ionic mechanism is proposed (*see* Scheme 5). In the first step, the elimination of acetic acid molecule affords the cation **8B**. There are two possible pathways of stabilization for this formed cation: **(a)** a proton elimination with alkene **20** (major route) formation, or: **(b)** a skeleton rearrangement, with cation **8D** formation, and its transformation in 9-methylphenanthrene (**21**) and phenanthrene (**22**) as secondary products.

In order to obtain more information related to the proposed carbenium ions intermediates (**8B**, **8C**, **8D**) formation, the MNDO semi-empiric calculations for the corresponding alcohol pyrolysis were run and presented in a previously work.[8] The cationic specie **8D** is theoretically demonstrated to be more stable, with 29 kcal/mole upper, then **8B** and **8C** resonance structures.[8]
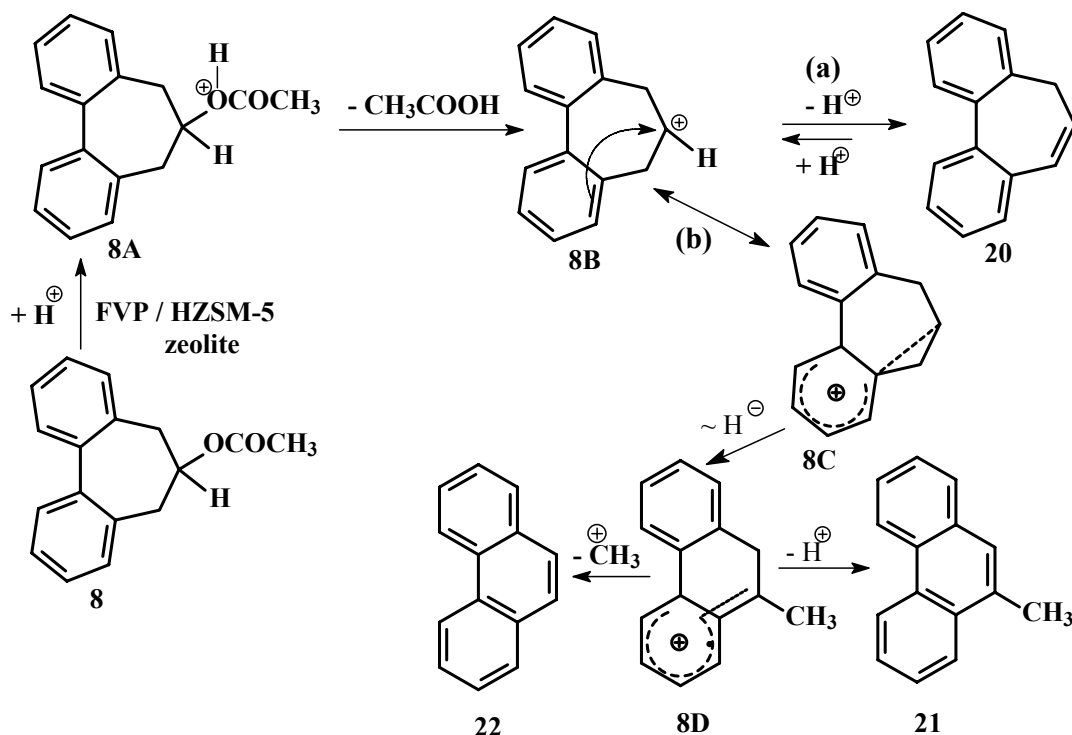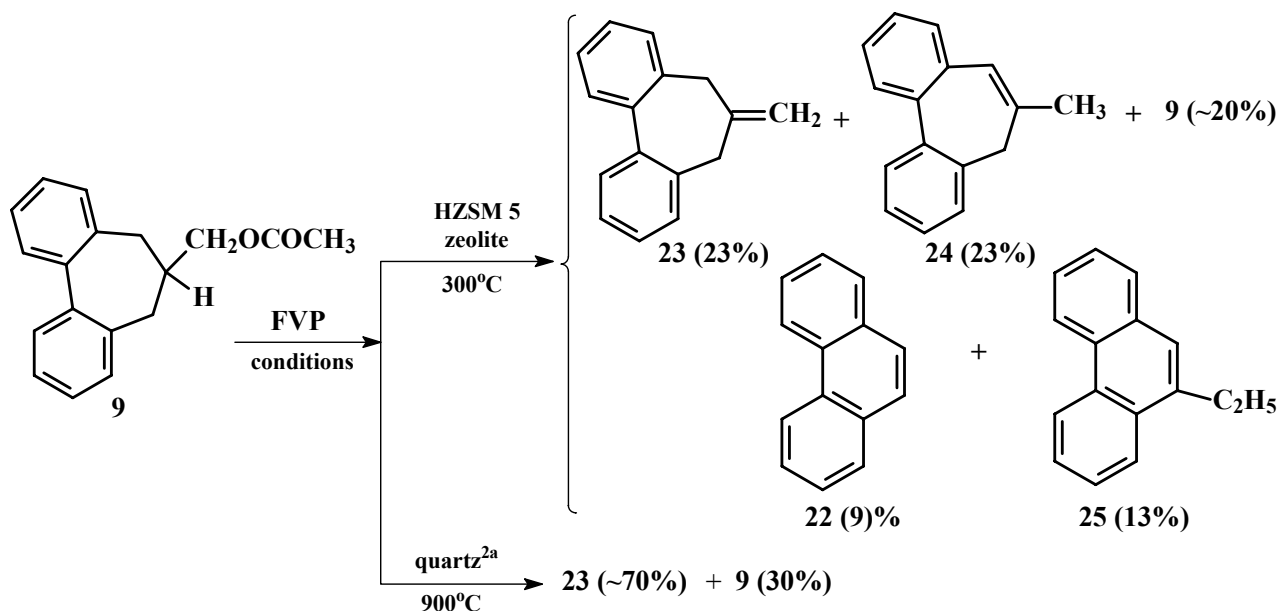

Scheme 5

2.3. Pyrolysis of 6-hydroxymethyl-6H-5,7-dihydrodibenzo[a,c]cycloheptene's acetate (9)
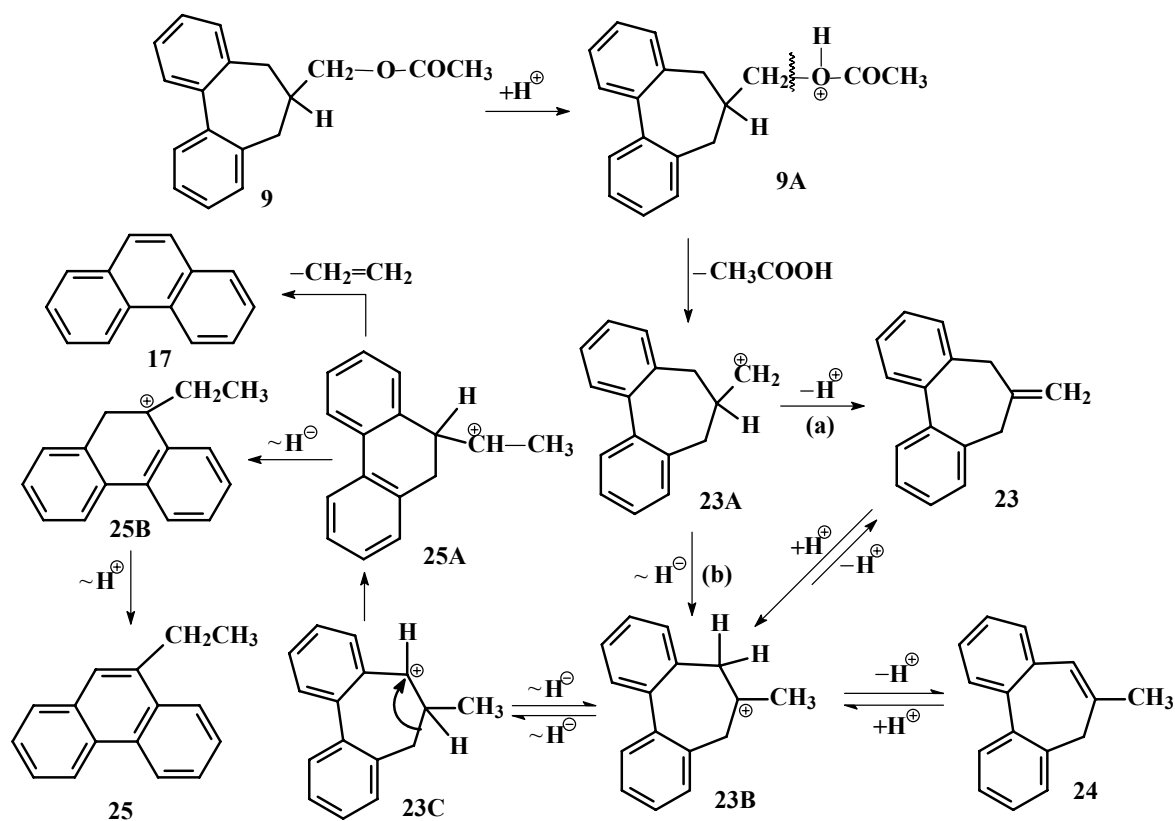
The thermal decomposition of acetate **9** in flow-vacuum conditions over HZSM-5 zeolite affords the reaction mixture (*see* Scheme 6): hydrocarbons

23 (23%), **24** (23%) and untransformed acetate **9** (~20%).

The proposed reaction mechanism of this thermal decomposition is presented in Scheme 7.

Scheme 6

Scheme 7

The acetate group protonation, followed by the acetic acid molecule elimination, occurs to the primary carbenium ion **23A**, which can be stabilized through two possible pathways: **(a)** by proton elimination with alkenes' **23** formation or: **(b)** by a hydride ion migration and the formation of the tertiary carbenium ion **23B.** This last mentioned ion existence explains the hydrocarbon **24**, the 9-methylphenanthrene (**21**) and phenanthrene (**22**) formation through the dibenzocycloheptane skeleton rearrangement.

In order to obtain more information related to the proposed carbenium ions intermediates (**23A-23C** and **25A**), the MNDO semi-empiric calculations[5b] were run (*see* Fig. 1).
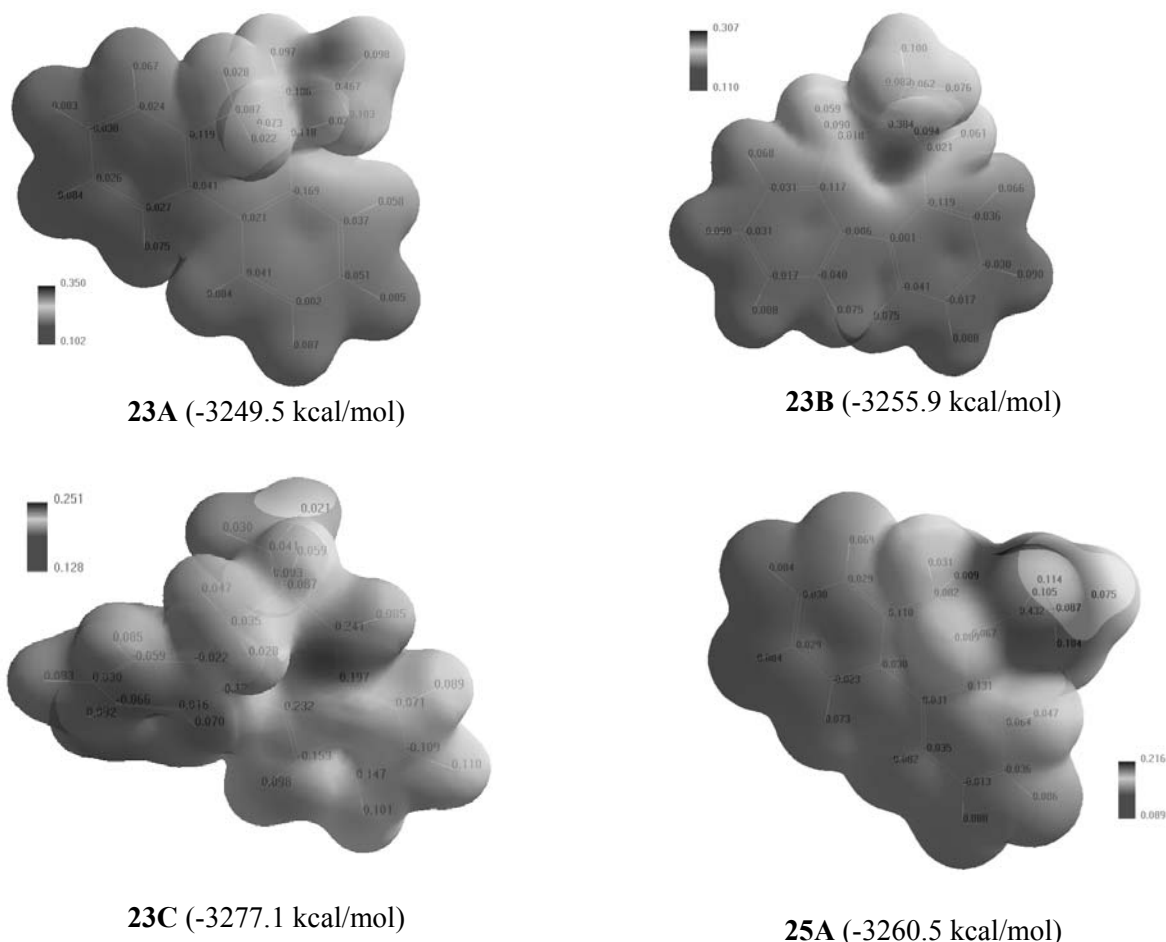

23A (-3249.5 kcal/mol)

23B (-3255.9 kcal/mol)

23C (-3277.1 kcal/mol)

25A (-3260.5 kcal/mol)

Fig. 1 – Calculated energy for the possible carbenium ions structures (at 300°C).

The carbenium ion **23A** is theoretically demonstrated to be more stable intermediate (with 27,6 kcal/mole upper than **23C,** with 11 kcal/mole upper than **25C** and with 6,4 kcal/mole upper than **23B** resonance structures). These obtained data explain the formation of the hydrocarbons **23** and **24** as major products (23%).

The alkene **23**, as main product was also obtained in the FVP of the acetate **9** over quartz, is stable at high temperatures (900°C). Regarding the same acetate **9**, the pyrolysis on zeolite catalyst promotes the protonation process, due to the acid medium, and explains the 9-methylphenanthrene (**21**) and phenanthrene (**22**) formation.

EXPERIMENTAL

General procedure of pyrolyses

The thermal decompositions were performed in flow-vacuum conditions, using a previously described apparatus (*see* Fig 2).[7] The pyrolysis glass tube (60 cm length, 10 mm inner diameter) was filled with HZSM-5 acid zeolite on 10 cm length and heated with cylindrical Nabertherm P330 vertical electric oven heaving temperature indicator and temperature programmer. The vacuum (0.1–0.2 Torr) was continuously measured with a Varian 801 vacuum gauge.

The acetate sample (35 mg) was sublimed under inert atmosphere (argon, flow rate 4 mL min.$^{-1}$) in the pyrolysis tube. The reaction products accumulated at the cooled end of the glass pyrolysis tube were dissolved in dichloromethane, the solvent was evaporated and the residue was analysed by

GC/MS. The temperature interval of thermal decompositions was between 250–350°C in order to avoid the radical conditions. Analytical pyrolyses at optimal temperature (when the starting acetate was totally or almost decomposed) were followed by preparative runs. The reaction products were identified by GC/MS using authentic samples or separated by liquid chromatography and their structures were confirmed by IR, ^{1}H- and ^{13}C-NMR spectroscopy.
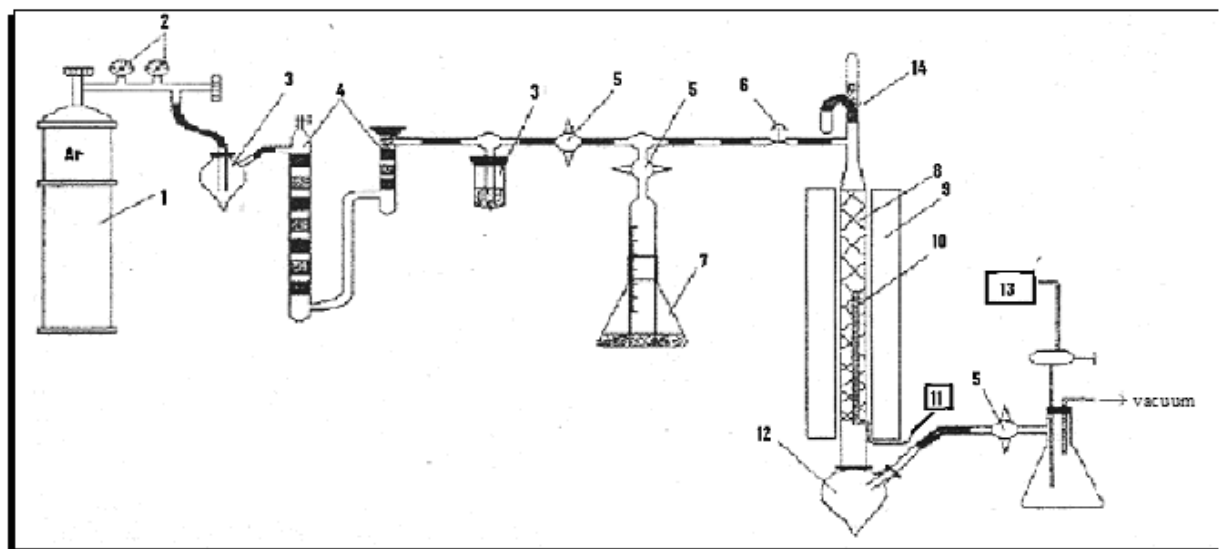

Fig. 2 – Flow-vacuum pyrolysis apparatus
1. argon tank; 2. pressure regulator; 3. bubble receivers; 4. dry tower; 5. taps; 6. valves; 7. argon flowmeter; 8. pyrolysis glass tube; 9. vertical electric oven; 10. thermocouple; 11. temperature controler; 12. products receiver; 13. vacuum gauge; 14. sample's introduction.

Apparatus for physical analyses

Melting points were determinate on a Boethius Kruss Optronic apparatus and are uncorrected. IR spectra were obtained with a FTIR Thermoelectron 6700 with micro ATR smart performer. The NMR spectra were registered on a Varian Gemini 300 apparatus at 300 MHz (^{1}H) and 75 MHz (^{13}C) using TMS as the internal standard. The GC/MS analyses were performed on an Agilent 6890 gas-chromatograph with split/split less injector, coupled with an Agilent 5975B mass-spectrometer provided with quadrupole. A DB5-MS capillary column Agilent 19091s-433 (length 30 m; 0.25 mm diameter, 7.04 psi initial pressure) was used. The analysis conditions were: injector temperature, 250 °C; split ratio, 30:1, carrier gas, hydrogen (flow rate, 1.2 mL min.[-1]); temperature of transfer-line, 250°C, electron ionization, 70 eV, masse range 46 – 550 u.a.m.

CONCLUSIONS

The flow-vacuum pyrolyses (FVP) of three acetates with a dibenzocycloalkane skeleton over HZSM-5 zeolite catalyst were performed. Due to the reaction conditions (temperature between 250-350°C, catalyst type) ionic reaction mechanisms were proposed in order to explain the products formation. For the corresponding acetates **7** and **9** the reaction mixture composition was different for the FVP reactions over quartz (at higher temperatures) *versus* over zeolite catalyst (at lower temperatures).

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