

FLOW-VACUUM PYROLYSIS OF DIBENZOCYCLOHEPTANE DERIVATIVES ON ZEOLITES CATALYSTS. IV¹

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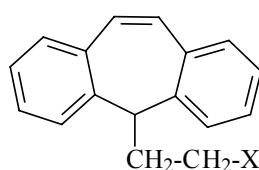
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The pyrolysis of 10,11-dihydro-5H-dibenzo[*a,d*]cicloheptadien-5-ol (**4**) and of 5H-dibenzo[*a,d*]cicloheptatrien-5-ol (**5**) in flow-vacuum conditions (advanced vacuum, inert atmosphere) on zeolites at 300°C is presented. The reaction products were identified by GC/MS using authentic samples and a reaction mechanisms involving cationic species as intermediates were proposed. A comparison with the pyrolysis of the same compounds performed in FVP conditions on quartz is presented.

INTRODUCTION

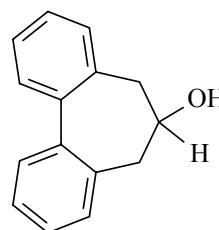
Very poor informations regarding the flow-vacuum pyrolysis (FVP) reactions of the dibenzocycloheptene systems (some alcohols: **1** –

3 and their corresponding acetates: **1**, **2**), in the presence of different acidic zeolites, in advanced vacuum and inert atmosphere, are presented in the literature.¹⁻³



1, 2

(X = - OH; - OCOCH₃)



3

In these reaction conditions, the formation of the resulted products is explained by a cationic mechanism, opposite to the radicalic one, observed when the same compounds (**1** - **3**) were pyrolyzed in a quartz tube^{4,5} at higher temperatures.

In this note we present the thermal behavior in FVP conditions on acidic zeolites catalysts of the two dibenzocycloalkanols: 10,11-dihydro-5H-

dibenzo[*a,d*]cicloheptadien-5-ol (**4**) and 5H-dibenzo[*a,d*]cicloheptatrien-5-ol (**5**).

The syntheses of the alcohols were performed by reduction of commercial corresponding ketones, with NaBH₄/NaOH in methanol (see **Scheme 1**).⁴

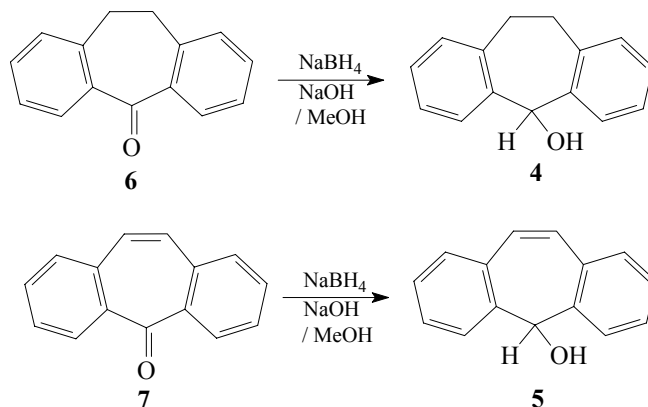
The FVP reactions of 10,11-dihydro-5H-dibenzo[*a,d*]cicloheptadien-5-ol (**4**) and 5H-dibenzo[*a,d*]cicloheptatrien-5-ol (**5**) were

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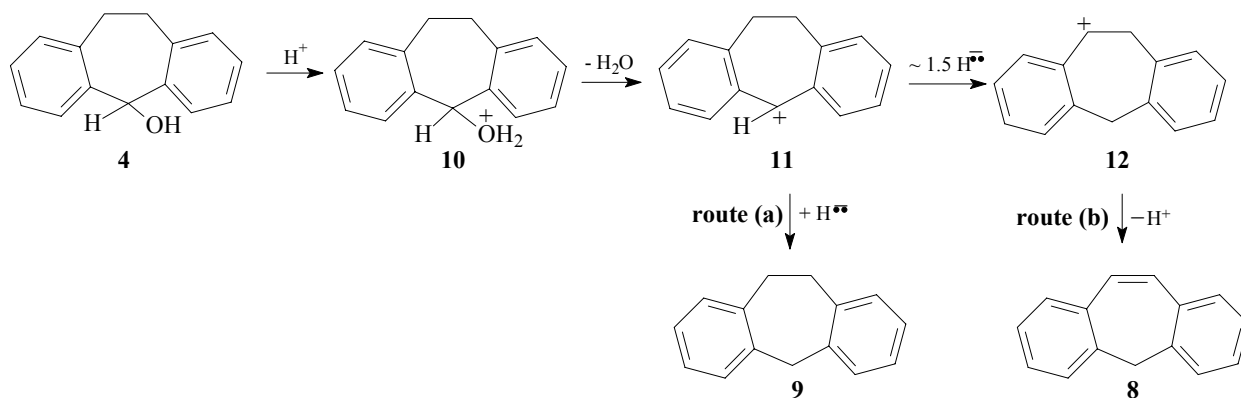
performed in an original apparatus, previously described.⁶

The flash-vacuum conditions were: advanced vacuum – 0.1 Torr; inert atmosphere – argon flow rate 4 mL/min; contact time – less than 0.25 s), in a

glass tube, acidic zeolites as catalyst (H-ZSM-5; β mesoporous zeolite), temperature 300°C (see **Scheme 2**). The resulted reaction mixture was analyzed by GC/MS.



Scheme 1



Scheme 2

Under the FVP reaction conditions on zeolites the alcohol 4 was transformed into a mixture of two hydrocarbons 8 and 9. Their formation can be explained through the cationic intermediates 11 and 12 appearance (see **Scheme 2**).

In order to obtain more informations related to the proposed cationic intermediates, the MNDO semi-empiric calculations⁷ were run (see **Fig. 1**).

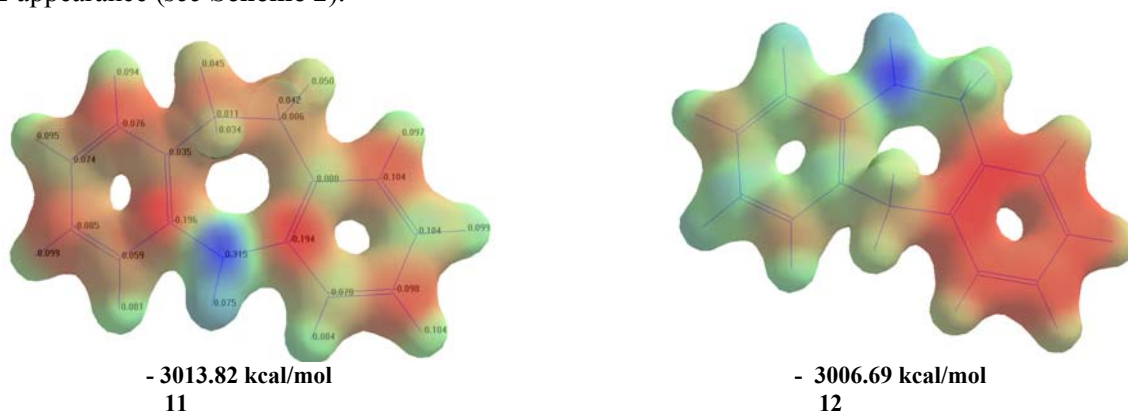


Fig. 1 – Calculated energy for the possible cationic structures (at 300°C).

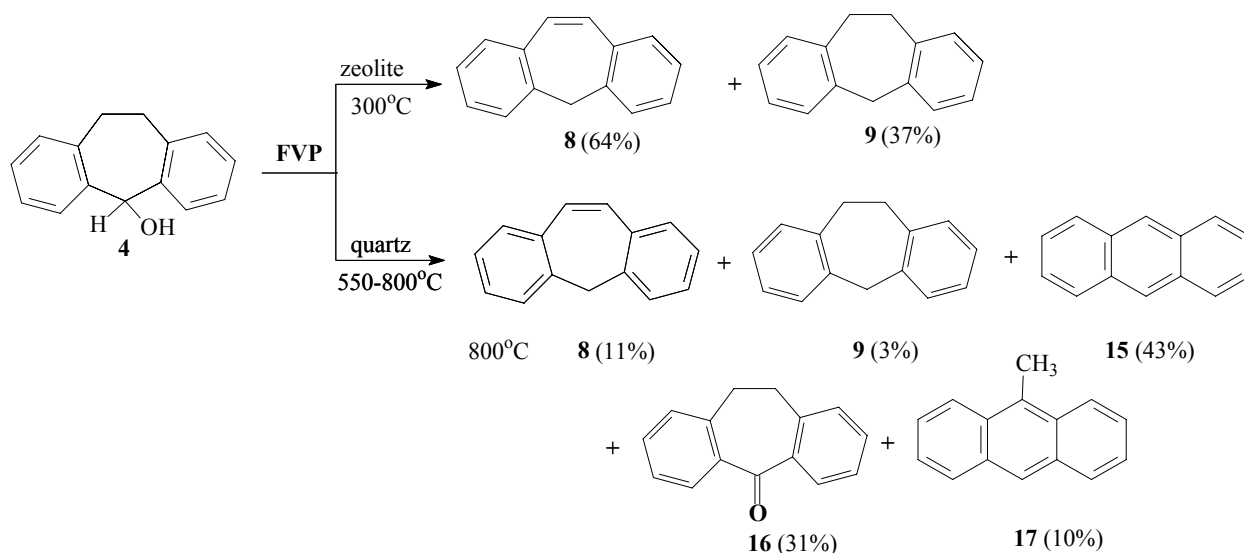
This calculation showed a high stability of the cation **11** in comparison with the cation **12**.

The alkene **8**, resulted from the unstable cation **12**, is the major reaction product due to the kinetic favorite **route b**.

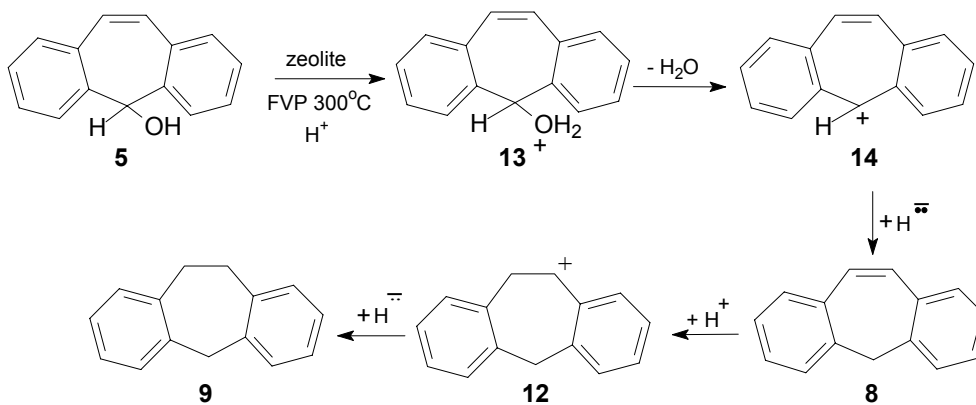
The FVP pyrolysis of the alcohol **4** on quartz conditions, ⁴ performed a more complex reaction mixture containing the same two hydrocarbons **8**

and **9** beside the anthracene (**15**), the methylanthracene (**17**) and the ketone **16**, explained by a radicalic mechanism. (see **Scheme 3**).

The same hydrocarbons **8** and **9** were obtained at the flow-vacuum pyrolysis on zeolites of the unsaturated alcohol **5**. A cationic mechanism (see **Scheme 4**) also explained their formation.



Scheme 3



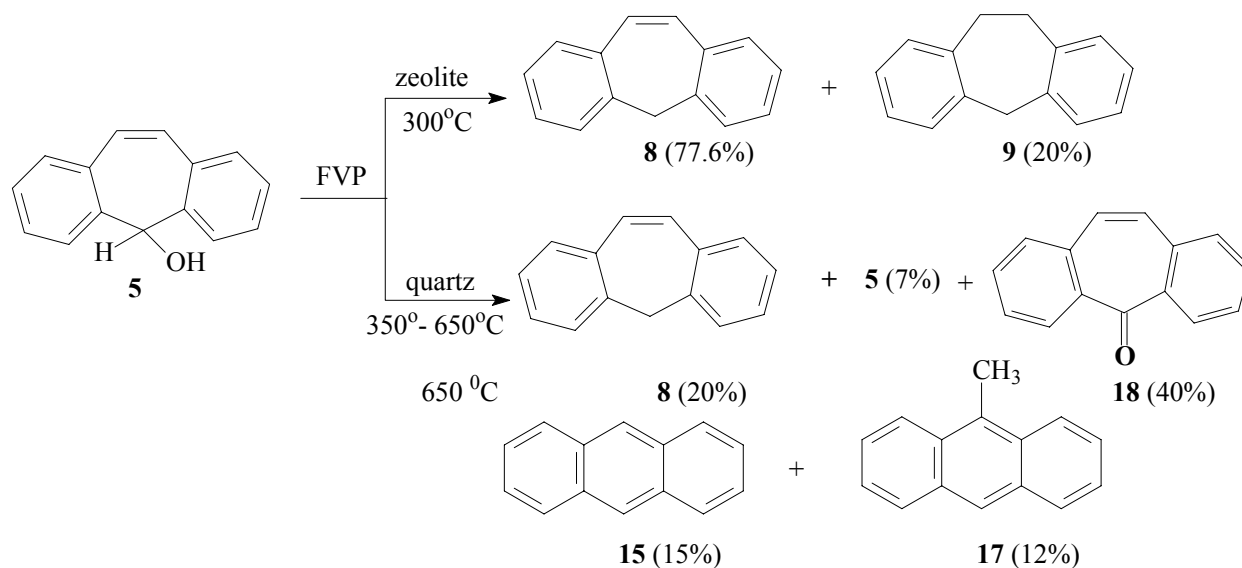
Scheme 4

A comparison between the FVP reactions performed on zeolites and on quartz conditions⁵ (with a radicalic mechanism) is presented in **Scheme 5**.

In conclusion, in this work the thermal decompositions in FVP conditions of the 10,11-dihydro-5H-dibenzo[*a,d*]cycloheptadien-5-ol (**4**) and 5H-dibenzo[*a,d*]cycloheptatrien-5-ol (**5**) on acid zeolites catalysts (H-ZSM-5; β mesoporous zeolite) at 300°C, were studied.

An ionic reaction mechanism is suggested in order to rationalize the formation of the obtained reaction products and a comparison between the results of the FVP reactions of the compounds **4** and **5** on acid zeolites catalyst and on quartz, was done.

The thermal stability of the alcohols **4** and **5** in FVP on zeolites conditions is lower than in FVP performed on quartz. The same hydrocarbons **8** and **9**, obtained in both cases, are the kinetic control products.



Due to the simplest reaction mixture, the thermal decompositions on zeolites at low temperature (300°C) seem to be more interesting than the reactions performed on quartz, not only for the synthetic reason but also for the environmental applications.

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