

FLOW-VACUUM PYROLYSIS OF DIBENZOCYCLOHEPTANE ANNELATED DERIVATIVE ON ZEOLITES CATALYSTS

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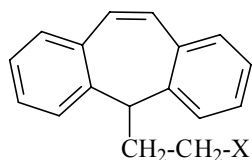
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The pyrolysis of 5H-6,7-dihydrodibenzo[*a,c*]cyclohepten-6-ol (**5**) in FVP conditions, a method of thermal decomposition in advanced vacuum, inert atmosphere on zeolites/acid Al₂O₃ at variable temperature between 300–350°C is presented. The reaction products were identified by GC/MS using authentic samples and a reaction mechanism involving cationic species as intermediates was proposed. A comparison with the pyrolysis of the same compound performed in FVP conditions on quartz is presented.

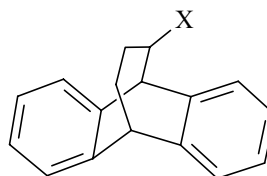
INTRODUCTION

The first flow-vacuum pyrolysis (FVP) reactions of dibenzocyclo-annelated systems (some alcohols and their corresponding acetates: **1** – **4**), in the

presence of different acidic zeolites, in advanced vacuum and inert atmosphere were performed some years ago by Banciu and co-workers:¹⁻³



1, 2 (X = - OH; - OCOCH₃)



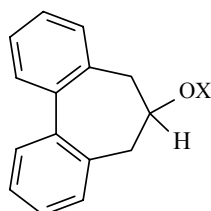
3, 4

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

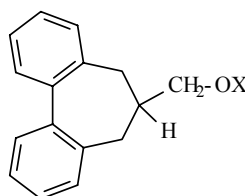
acetates (e.g. **5**¹, **6**⁶, **7**⁶, **8**⁷, **9**⁶ and **10**⁶) was studied in FVP reactions conditions on quartz.

The thermal behavior of some related dibenzocycloalkanols and their corresponding

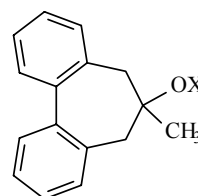
The formation of all reaction products, identified in the obtained reaction mixtures, was explained through radical mechanisms also.



5 X=H
8 X= Ac



6 X=H
9 X= Ac



7 X=H
10 X=Ac

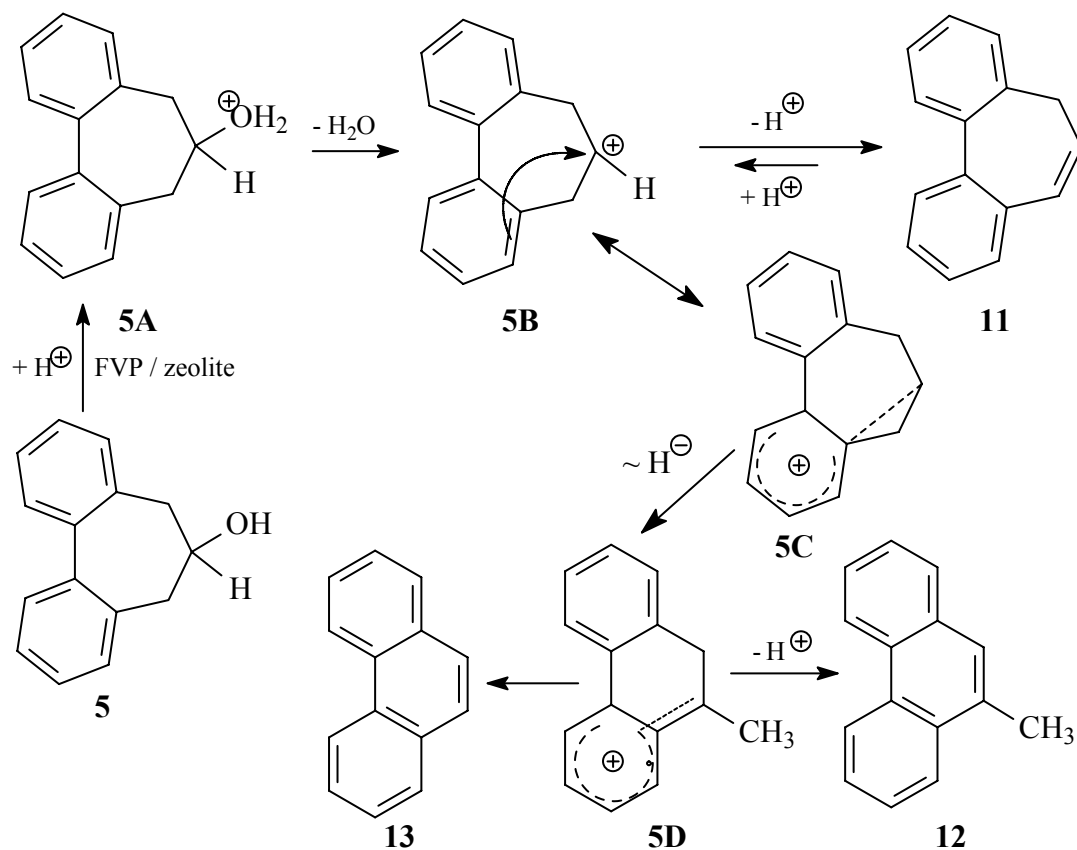
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Three of the products (**11**, **12** and **13**) were identified in the reaction mixture from the FVP in quartz conditions also.

The formation of the main products in the pyrolysis reaction on zeolite catalyst for the studied alcohol **5** is explained through an ionic mechanism (see Scheme 4). In the mentioned conditions, the alcohol **5** is protonated to **5A**. The cationic intermediate **5B**, resulted by dehydration of **5A**, is stabilized through deprotonation to the unsaturated hydrocarbon **11** (major product). The possible reversibility of the deprotonation step was

verified through FVP of **11**, in similar conditions. The higher yields of the unsaturated hydrocarbon **11**, obtained in FVP on zeolites of alcohol **5**, can be explained by the thermal stability of this compound (its thermal decomposition, in quartz tube, was observed at temperatures over 600°C¹).

The cationic intermediate **5C**, resulted by conjugation of **5B** (equal energy calculated system) is stabilized through ring rearrangement to the more stable cationic intermediate **5D**, which generates the products **12** and **13**.



Scheme 4

In order to obtain more information related to the proposed cationic intermediates, the MNDO semi-empiric calculations¹⁰ were run (see Fig. 1). The cationic specie **5D** is theoretically demonstrated to be more stable, with 29 kcal/mole upper, than **5B** and **5C** resonance structures.

In conclusion, in this work it was studied the thermal decomposition in FVP conditions of 5H-6,7-dihydrodibenzo[*a,c*]cyclohepten-6-ol (**5**) on acid zeolites catalysts (H-ZSM-5; Montmoryllonite K10/ Al_2O_3 / HNO_3) at 300-350°C. The formation of 5H-dibenzo[*a,c*]cycloheptene (**11**), as main pyrolysis reaction product in such conditions, is

explained by its thermal stability at low temperature, observed also in FVP reaction performed on quartz.¹

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 compound **5** on acid zeolites catalyst and on quartz, was done.

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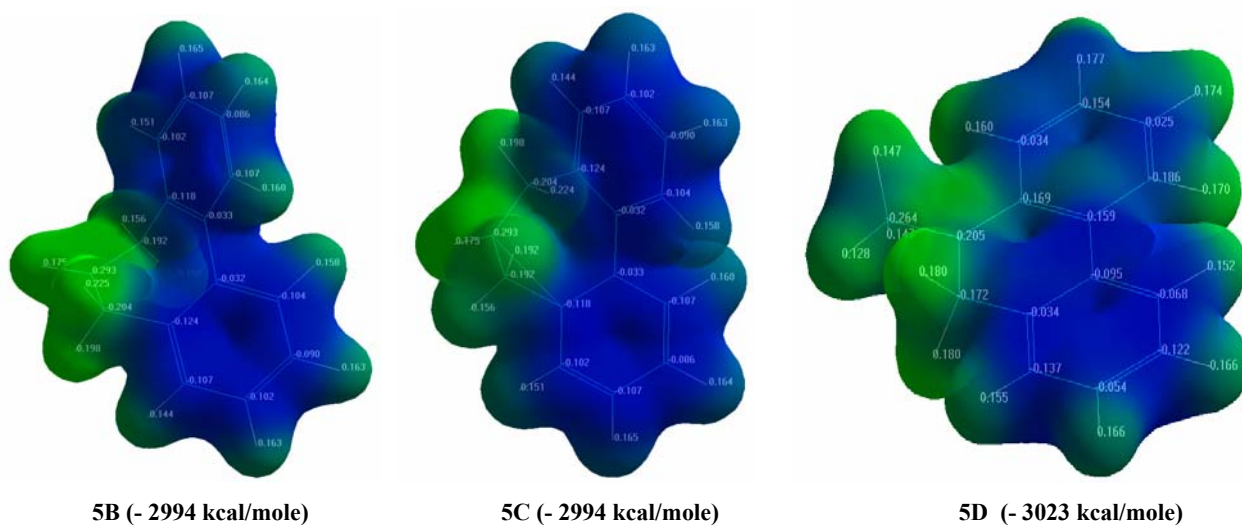


Fig. 1 – Calculated energy for the possible cationic structures (at 300°C).

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