

Flash-Vacuum Pyrolyses on Zeolites. 5 [1]

Pyrolysis of the 5β-(tosylethyl)-5h-dibenzo[a,d]cycloheptatriene

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The pyrolysis in a flow vacuum system on zeolites (HZSM 5, mezoporous β zeolite) and inert atmosphere (argon, 4 mL/min.) of the 5β-(tosylethyl)-5h-dibenzo[a,d]cycloheptatriene (**1**) is presented. The resulted reaction mixtures were analyzed by GC/MS and compared with authentic samples. In order to rationalize the obtained products distribution, ionic mechanism explaining the formation of the main reaction products was suggested and a comparison between the solvolysis of the same compound was done.

Keywords: flash-vacuum pyrolyses, zeolites, dibenzocycloalkane tosylate

The flow-vacuum pyrolysis (FVP) reactions are interesting to their use in synthesis of organic derivatives and also for their applications in controlled destruction of toxic compounds. The FVP reactions of the derivatives with dibenzocycloalkane skeleton on zeolites represent a new developed field in the last years [2-4]. The ionic reaction mechanism, in comparison with the radicalic one of the FVP on quartz conditions, is a new and interesting domain for our research group.

There interest for these polycyclic systems is justified by their potential biological activity.

Experimental part

Melting points are uncorrected. IR spectra were registered on a Bruker Equinox 55 spectrometer. The NMR spectra were registered at 300 MHz (¹H-) and 75 MHz (¹³C) on a Varian Gemini 300 apparatus using TMS as internal standard. The GC/MS analyses for pyrolyses of compound **1** 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 analyses 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.

Synthesis of tosylate **1**

The tosylate **1** was obtained from the corresponding alcohol **2** by reaction with the tosyl chloride in anhydrous pyridine [5] (scheme 1).

A mixture of 0.5 g (2.2 mmoles) of alcohol **2** and 5 mL of anhydrous pyridine is added in an Erlenmeyer flask and cooled on ice. 0.45 g (2.6 mmoles) of tosyl chloride is added in small portions, under permanent stirring, over the mixture, until complete solubilization. The resulted reaction mass is kept over ice for 24 h, then is poured over 50 mL of water-ice and the tosylate **1** precipitates. The product is purified by recrystallization from ethyl alcohol and the reaction yield was 85% (m.p. = 144 °C).

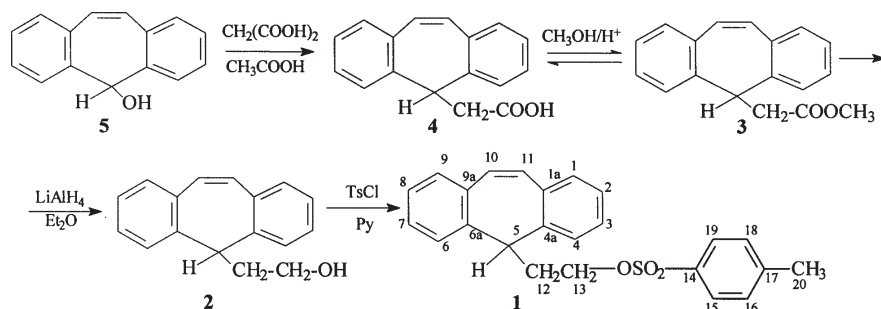
The synthesis of alcohol **2** was performed by literature data [3, 5]. The alcohol **5** was obtained from Merck dibenzosuberone by reaction with sodium borohydride in methanol.

The spectral data for the tosylate **1** are presented as follows:

IR spectrum (KBr, ν, cm⁻¹): 552 i; 656 m; 763 i; 912 i; 984 m; 1163 i; 1346 i; 1595 i; 2851 i; 2922 m; 2961 i; 3017 i; 3062 i. with *i* - intense; *m* - medium.

¹H-NMR spectrum (CDCl₃, δ, ppm; J, Hz; iz. axial MAJOR): 2.00 (dt; 8,0; 5.8; 2H; H¹²); 2.43 (s; 3H, H²⁰); 3.66 (t; 5.8; 2H; H¹³); 4.12 (t; 8.0; 1H, H³); 6.83 (s; 2H, H^{10, 11}); 7.10 – 7.35 (m, 10H; H¹⁻⁹, H¹⁶, H¹⁸); 7.72 (d; 8.2; 2H; H^{15, 19}).

¹³C-NMR spectrum (CDCl₃, δ, ppm; J, Hz; iz. axial MAJOR): 21.72 (C²⁰); 29.15 (C¹²); 50.13 (C⁵); 68.66 (C¹³); 126.75 (CH); 128.81 (CH); 128.91 (CH^{15, 19}); 129.85 (CH); 129.91 (CH); 130.03 (CH); 130.87 (CH^{10, 11}); 134.02 (C^{1a, 9a}); 139.47 (C^{4a, 6a}); 144.73 (C¹⁷).

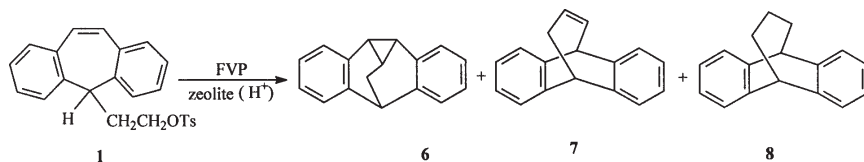


Scheme 1

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Table 1
CHARACTERISTICS OF THE ZEOLITE CATALYSTS (ACID ZEOLITES)

Zeolitic catalyst	Molar ratio SiO ₂ / Al ₂ O ₃	Atomic ratio Si/Al	Langmuir specific surface m ² g ⁻¹	Volum of pores cm ³ g ⁻¹
HZSM-5	20	40	485	0.16
Mezoporous β zeolite	200	400	374	0.38



Scheme 2

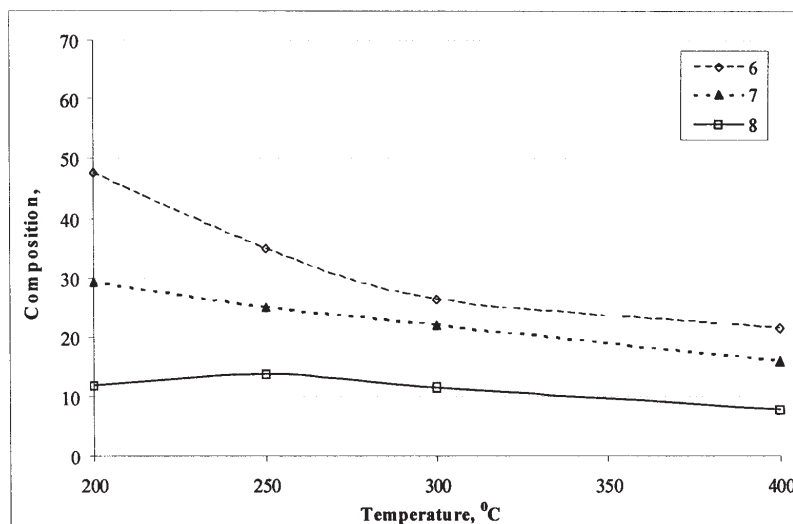


Fig. 1. Reaction products distribution

General procedure of pyrolyses

In the present work, we studied the thermal behaviour of the tosylate **1** in FVP reaction on acid zeolites. The surface acidic properties of the catalysts were determined through chemisorption of ammonia followed by programmed thermodesorption in a flow-system. The main characteristics of the zeolite catalysts are presented in table 1.

The pyrolyses were performed in an original apparatus [6], in flash-vacuum conditions (advanced vacuum – 0.1 Torr; inert atmosphere – argon flow rate 4 mL/min; contact time – less than 0.25 s), in a glass tube, acid zeolites as catalyst and temperature range between 200 and 400°C. The reaction mixtures, as a yellow solid deposits, were dissolved in chloroform, the solvent was evaporated and the solid residues were GC/MS analyzed, using authentic samples of hydrocarbons **6** – **8**.

Results and discussions

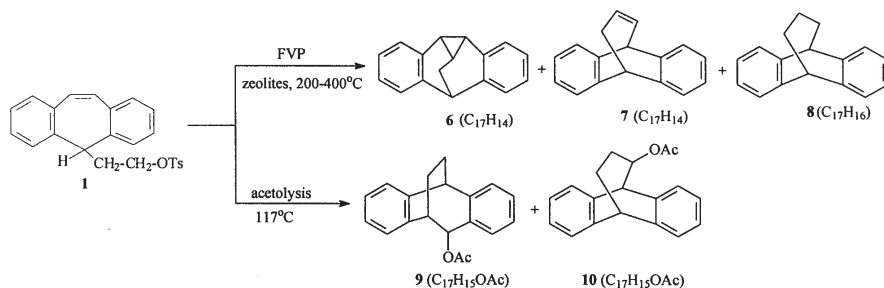
The major reaction products were the hydrocarbons **6**, **7** and **8** (scheme 2), present as main reaction products in the entire temperature interval studied in this work (200 –

400°C). However, their distribution varies with temperature (fig. 1). Thus, the formation of hydrocarbon **6** decreases rapidly with increasing temperature, whereas the proportion of **7** decreases slowly. The formation of the saturated hydrocarbon **8** increases visibly in the interval 200 – 250°C, but decreases imperceptible after 250°C.

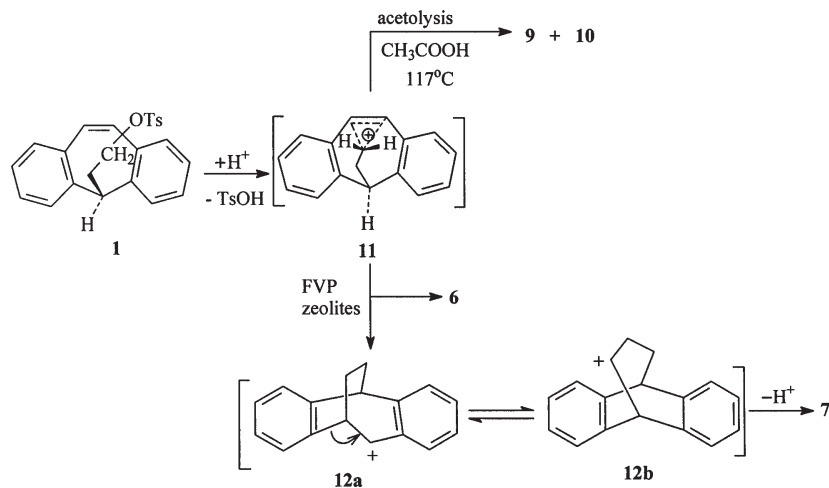
The products distribution in the studied temperature interval shown in figure 1 may indicate that **6** is the initial reaction product. The unsaturated hydrocarbon **7** (isomeric with **6**) must result by a structural rearrangement of the initially formed hydrocarbon, whereas **8** results from **7** by hydrogenation. These conclusions may lead to the scheme 3.

The formation of the polycyclic hydrocarbons **6** – **8** has some similarity with the products resulted in the acetolysis of **1** [5].

Thus, the acetate **10** resulted in acetolysis from tosylate **1** has the same skeleton with hydrocarbons **7** and **8**, formed in pyrolysis, suggesting similar steps in the transformation of the tosylate **1** in both processes. As was proposed before [5], the initial step must be the formation of the ion pair **11**, resulted with the direct participation of the double bond in



Scheme 3



Scheme 4

the ionization of the tosylate (scheme 4).

In acetolysis, the ion pair **11** is rapidly transformed into acetates **9** and **10**, whereas in pyrolysis process, the initially formed ion pair **11** yields either hydrocarbon **6**, or rearranges into ions **12a** and **12b**. The latter ion (**12b**) is responsible for the formation of hydrocarbon **7** (by proton elimination) or **8** (by hydride ion transfer).

In order to obtain more information related to the proposed cationic intermediates, the MNDO semi-empiric

calculations [8] were run (fig. 2).

We have also observed that in flash-vacuum pyrolyses of tosylate **1** performed on pure acid zeolites (HZSM 5 and mezoporous β zeolite) only the formation of the isomeric hydrocarbons **6** and **7** as main products without a significant detection of the saturated hydrocarbon **8**.

We compared these results with the results of the FVP reactions of the corresponding alcohol and acetate performed on acid zeolites catalysts with aluminum oxide, (30 % HZSM 5 / 70% Al_2O_3) when the reaction mixture contains as major products benzo[*c*]fluorene (**14**) and benzo[*a*]fluorene (**21**) [2,3] (scheme 5 and 6).

The formation of these polycyclic hydrocarbons can be explained starting either from the tosylate **1**, or from the principal reaction products **6** and **7**, which all generate ion **11**. This ion is a derivative of the protonated cyclopropane [7]. It has been shown that substituted protonated cyclopropanes can be isomerized by proton migration from the pentacovalent carbon atom to the vicinal carbon atom of the system (fig. 3).

In previous paper [2, 3] the zeolites catalytic surface activity for dibenzocycloheptatriene derivatives in FVP reactions, was proved.

In order to obtain more information about the reaction mechanism, the pure mezoporous β zeolite was used as catalyst in study of thermal behaviour of tosylate **1**. Unfortunately, we obtained the same reaction products distribution as in presence of the HZSM 5 zeolite catalyst with micropores. This fact is probably an effect of the very short contact times when FVP take place only on the surface of the catalysts, but the reaction mechanism includes the formation of cationic species stabilized by

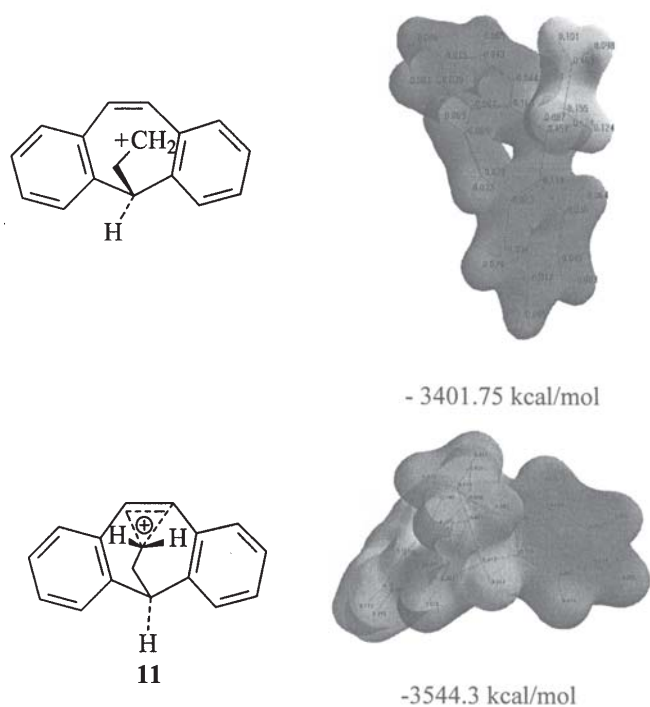
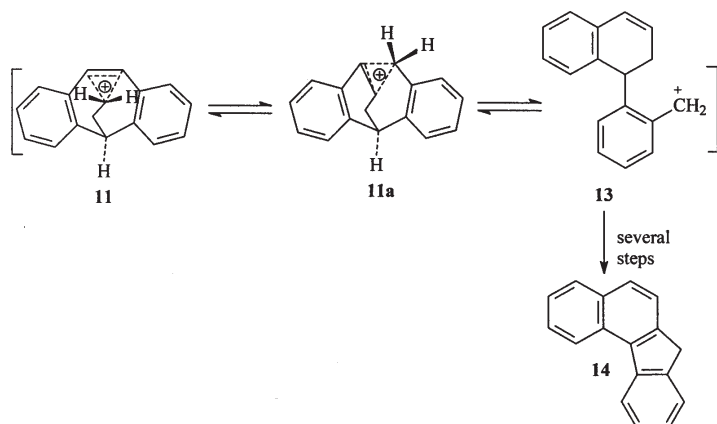
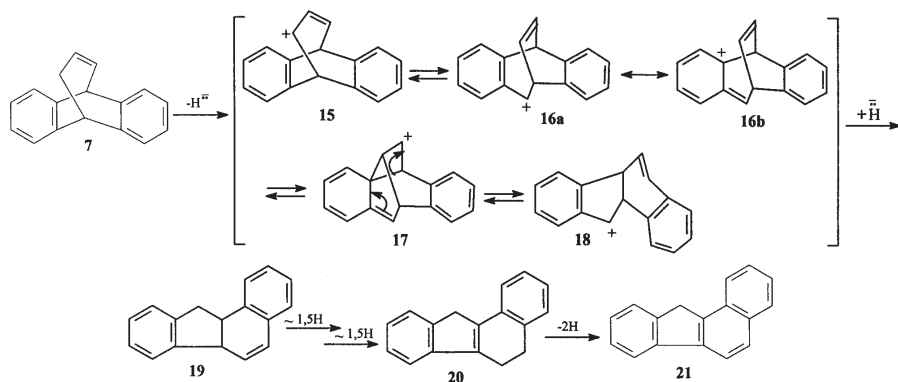


Fig. 2. MNDO semi-empiric calculations for the carbenium ions:
 a) primary carbenium ion; b) protonated cyclopropane (11)



Scheme 5



Scheme 6

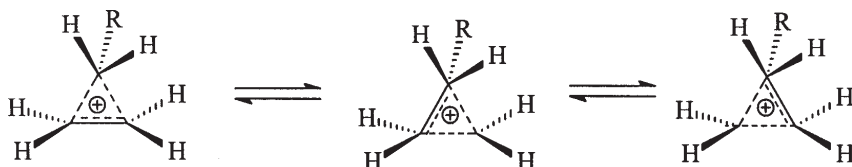


Fig. 3. Isomerisation of the corner protonated cyclopropanes

proton elimination.

Also, it was observed that in FVP reactions performed on quartz conditions at higher temperatures ($t > 400^\circ\text{C}$) rearrangements and aromatization processes take place. [9, 10]

However, in these reactions a hemolytic mechanism was assumed.

Conclusions

In this work we have presented:

- the spectral characterization of the 5 β -(tosylethyl)-5H-dibenzo[*a,d*]cycloheptatriene (**1**), synthesized by literature data;

- the thermal behaviour of the tosylate **1** in flash-vacuum pyrolysis on pure acid zeolites when were formed only the isomeric hydrocarbons **6** and **7** as kinetic controlled products;

- in order to explain only the formation of hydrocarbons **6** and **7** on pure zeolite catalyst, we suggested a ionic mechanism with formation in the initial step of a corner protonated cyclopropane **11**, generating hydrocarbon **6**, or passing over in other unstable cationic species, generating the other observed products;

- the FVP of the tosylate **1** on pure acid zeolites seems to take place on the surface of the catalysts, probably as the effect of very short contact times (the same fact was observed for the FVP of the corresponding alcohol and acetate on zeolites at 350°C) [2, 3].

Acknowledgements: This research work was financed by the Ministry

of Education and Research of ROMANIA, Grant 1557/2009. The authors thank Mrs. Phd. Eng. Cristina Florea from "C.D. Nenitzescu" Institute of Romanian Academy for a sample of the mixture of the isomeric hydrocarbons **6** and **7**.

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Manuscript received: 9.06.2010