Flow-Vacuum Pyrolysis of Polycyclic Compounds. 26 [1]
Pyrolysis of Some Acetates with Dibenzocycloalkane Skeletons

DANIELA ISTRATI1*, ANGELA POPESCU1, LUMINITZA PARVULESCU1, ELENA ANDREI1, CONSTANTIN DRAGHICI1,
CRINU CIUCULESCU2
1 Politehnica University of Bucharest, Department of Organic Chemistry, 313 Splaiul Independentei, 060042, Bucharest, Romania
2 "C.D. Nenitzescu" - Institute of Organic Chemistry, Romanian Academy, 202B Splaiul Independentei, 060023, Bucharest, Romania

The syntheses and flow-vacuum pyrolyses of 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-acetate (7), 10,11-
dihydro-12H-dibenzo[a,f]cycloocten-5-acetate (8) and 5H-6,7-dihydrodibenzo[a,c]-cyclohepten-6-acetate (9) were presented. The products' distributions were determined by GC/MS and a reaction mechanism involving radical species was suggested, in order to explain the formation of the main reaction products.

Keywords: flow-vacuum pyrolyses, GC/MS, dibenzocycloalkane skeletons

In our previous papers we described the thermal behaviour in flow-vacuum pyrolysis (FVP) of the dibenzocycloankanols [2-5] such as: 1-2 [2], 3 [3], 4 [4], 5 [5] with dibenzocycloheptene skeleton and of some related acetates 6a,b [2] (fig. 1):

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

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

In order to obtain new evidence concerning the reaction mechanisms for dibenzocyclo-alkane derivatives, we present herein the thermal behaviour in flow-vacuum pyrolysis of three new dibenzocycloalkane acetates: 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-acetate (7), 10,11-
dihydro-12H-dibenzo[a,f]cycloocten-5-acetate (8) and 5H-6,7-dihydrodibenzo[a,c]-cyclohepten-6-acetate (9) (fig. 2).

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 compounds 7 - 9 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.

* e-mail: d_istrati@yahoo.com

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Synthesis of acetate 7

A mixture of 2.1 g (10 mmol) alcohol 3, 70 mL acetic acid (100%) and 2 g (20 mmol) malonic acid was refluxed for 24 h. Acetic acid was distilled with water and extracted with ethyl ether. The organic layers were washed with water (pH = 5-6), dried with anhydrous magnesium sulfate. After the solvent evaporation and recrystallization from methyl ethyl ether, the acetate 7, as white crystals, is obtained (\( \eta = 90\% \); m.p. 82\(^\circ\)C).

Synthesis of acetate 8

The synthesis of acetate 8 was performed in the same conditions as previous acetate, from corresponding alcohol 5. It was obtained a dark brown solid; after purification by column chromatography (silica, benzene as eluent) light brown crystals with m.p. 106-107\(^\circ\)C (\( \eta = 65\% \); m.p. 96\(^\circ\)C).

Synthesis of acetate 9

The acetate 9 was prepared from the corresponding alcohol 4 in 15 mL pyridine, at 0\(^\circ\)C, with 5 mL of acetic anhydride, under magnetic stirring. The reaction mixture was maintained 24 hours at 50\(^\circ\)C. After vacuum evaporation of pyridine, 20 mL 5% hydrochloric acid solution were added. The mixture was extracted with chloroform. The organic layers were washed with 5% hydrochloric acid solution and then with water until neutral. The acetate 9 was obtained after solvent evaporation as white-yellow crystals (\( \eta = 65\% \); m.p. 96\(^\circ\)C).

IR spectrum (CH\(_2\)Cl\(_2\), v, cm\(^{-1}\)): 750i, 1031m, 1087m, 1245i (\( \nu_{C=O} \)), 1400m, 1735i (\( \nu_{C=O} \)).

1H-NMR spectrum (CDCl\(_3\), \( \delta \), ppm): 2.57 (s, 3H, \( H_{13} \)); 2.91 (s, 1H, \( H_{11} \)); 7.1-7.27 ppm (4H, \( H_{4,6,8,9} \)).

13C-NMR spectrum (CDCl\(_3\), \( \delta \), ppm): 39.97 (C\(_9\)); 41.11 (C\(_7\)); 43.79 (C\(_6\)); 70.89 (C\(_5\)); 123.87 (C\(_3\)); 127.22 (C\(_2\)); 127.72 (C\(_1\)); 130.60 (C\(_10\)); 138.73 (C\(_8\)); 142.18 (C\(_7\)); 170.19 (C\(_12\)); 170.57 (C\(_1\)).

MS spectrum (m/e, relative abundance %): 63 (1); 83 (1); 115 (2); 139 (1); 163 (2); 164 (1); 165 (15); 166 (9); 167 (2); 176 (3); 177 (1); 178 (12); 179 (1); 180 (2); 189 (5); 190 (3); 191 (31); 192 (100; P.B.); 193 (32); 194 (4).

General procedure of pyrolyses

For a good correlation of experimental data between the previous and present results we performed the flow-vacuum pyrolyses of dibenzocycloalkane derivatives 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 (1-2 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 GC/MS analysed (See Experimental). Analytical pyrolyses at optimal temperature were followed by preparative runs either in order to isolate the main products or for spectra registration.

Results and discussions

The acetates 7 and 8 were obtained in a special way from the dibenzocycloalkanols 3 and 5 with acetic acid in the presence of malonic acid [8] (scheme 1). The usual conditions (acetic anhydride in pyridine) were unable to transform these alcohols into their corresponding acetates.

The acetate 9 was prepared from the corresponding alcohol 4 with acetic anhydride in pyridine, at room temperature (scheme 2) (part experimental):
The syntheses of ketones 11 and 12 were performed using literature data [9] and [10] respectively.

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

The compound 7 is very stable: at 600°C it was scarcely converted (~1%) and only at 900°C it was completely transformed. The main products (of the very complex mixture) resulted in these pyrolyses are presented in Scheme 3.

Pyrolysis of 10,11-dihydro-12H-dibenzo[a,f]cycloocten-5-acetate (8)

The acetate 8 was pyrolysed between 600°C – 925°C and the products distribution is presented in scheme 4.

Pyrolysis of 5H-6,7-dihydrodibenzo[a,c]cyclohepten-6-acetate (9)

The acetate 9 was pyrolysed between 450°C – 800°C and the main products are presented in Scheme 5.

A rationalization of the experimental data is proposed in the mechanistic Schemes 6-8.

The proposed radical mechanism for pyrolysis of 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-acetate (7) is presented in scheme 6.

In the route a) a radical break of CH₂ – CH₂ bond in 7 affords the benzyl diradical 7A. By elimination of acetate radical the benzyl radical 7B is formed. It can be converted to spirane 24. A thermally allowed intramolecular [π₂s+σ₂s+σ₂s] process in spirane compound 24 leads to dihydroanthracene (25) and anthracene (15). In the route b) by acetate radical elimination the benzyl radical 7D can be formed. It may be stabilised to alkene 13, which at high temperature decomposes and affords 9-methylanthracene (14) and anthracene (15) [11]. A radical break (route c) of the O - COCH₃ bond followed by hydrogen atom elimination affords the ketone 10, which is decarbonilated.
[6] over 700°C with formation of dihydrophenanthrene (26) and finally phenanthrene.

The rationalization of the thermal behaviour of the acetate 8 (10, 11-dihydro-12H-dibenz[a,f](cycloocten-5-acetate) in flow-vacuum pyrolysis is presented in scheme 7.

Elimination of the acetate radical affords the dibenzyl radical 8A which can be stabilized with formation of alkene 16 and the minor dibenzocycloalkane 17. Over 750°C the alkene 16 is transformed by two routes [a) and b)] with formation of stable compounds: anthracene (15), vinylanthracene (18) and the hydrocarbon 19 as main products.

In scheme 8 it is proposed the radical mechanism of the thermal decomposition in FVP conditions for 5H-6,7-dihydrodibenzo[a,c]cycloheptene-6-acetate (9).

The break of the acetate (OCOC<sub>2</sub>H<sub>5</sub>) radical generates the secondary radical 9A which is converted into alkene 21 by hydrogen atom elimination. At higher temperature, this alkene is transformed in stable aromatic hydrocarbons [12]: 9-methylphenanthrene (22) and phenanthrene (23). In the route b the break of the acetyl radical generates the radical 9B, which may be stabilized with formation of the ketone 13: at high temperature, by decarbonilation of ketone 13 and dehydrogenation of dihydrophenanthrene (26), phenanthrene (23) is formed, as stable aromatic product.

**Conclusions**

In conclusion, in this work we have presented:
- the synthesis and spectral characterization of three acetates (7-9) with annelated dibenzocycloalkane skeleton;
- the thermal behaviour in flow-vacuum pyrolysis of these acetates;
- the main reaction products and radical mechanisms of conversion were proposed;
- the pyrolysis of the new acetates (7-9) with dibenzocycloalkane skeleton confirmed the previous results [7] involving acetic acid elimination.
- the mechanisms previously suggested involved the radicals' generation, which affords as final stable compounds, aromatic hydrocarbons, such as 9-methylanthracene, anthracene and phenanthrene.
Acknowledgements: This work was partly supported by a CNCSIS Grant 78/5-2007

References

Manuscript received: 4.02.2008