THERMAL BEHAVIOUR OF SOME DIBENZOBICYCLO[2.2.2]OCTANE DERIVATIVES

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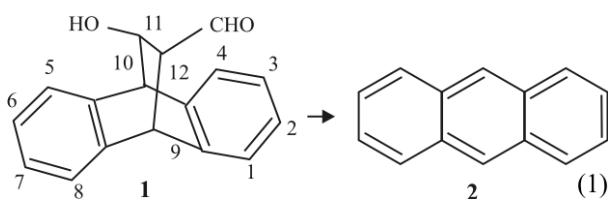
A number of dibenzobicyclo[2.2.2]octane derivatives have been studied due to the interest of such compounds as ligands for coordination compounds with potential biological activity. Their thermal behaviour has been analyzed in order to find out more information about their fragmentation. A connection between the bridge substituents and the fragmentation process has been observed.

Introduction

The compounds with a dibenzobicyclo[2.2.2]octane skeleton are of interest due to their potential biological activity. In previous papers [1–4] a number of compounds with such skeleton have been studied and it has been shown that they are polydentate ligands. Their coordination compounds present in the same time two moieties with possible biological activity, the ligand and the transitional metal. Among the properties of such compounds their thermal behaviour has to be studied in order to observe their stability as well as the way of decomposing.

The thermal behaviour of the hydroxy aldehyde **1** was presented before [5]. The ligand **1**, as well as its coordination compounds decomposed mainly by a retro-diene reaction (1) generating anthracene.

Taking in account this thermal behaviour it seems of interest to synthesize and study new compounds having a dibenzobicyclo[2.2.2]octane skeleton.

Experimental

The synthesis of the compounds 4-6 was performed as previously described [4]. The IR spectra of the compounds were recorded with a K, Zeiss Jena UR 20 spectrophotometer, and the NMR spectra with a Gemini 300-Varian (with internal TMS) apparatus.

Dimethyl ester of $_{trans}$9,10-dihydro-9,10-ethano-anthracene-11,12-dicarboxylic acid 3

A cream-white solid was isolated after recrystallization from methanol, m.p. 106–107°C (55% yield) [6].

IR spectrum (CCl_4, cm^{-1}): 880 w, 980 w, 1020 w, 1150 m, 1180 m, 1195 $s_{(C-O)}$, 1450 m, 1480 w, 1730 $vs_{(C=O)}$, 2980 m, 3020 w.

^{13}C NMR spectrum ($CDCl_3$, ppm): 172.8 (C=O); 142.09 (C_{8a}); 140.38 (C_{4a}); 126.50 (C_2,C_6); 126.42 (C_3,C_7); 124.54 (C_4,C_8); 123.83 (C_1,C_5); 52.32 (CH_3); 47.88 (C_9,C_{10}); 46.73 (C_{11},C_{12}).

Dihydrazide of $_{trans}$9,10-dihydro-9,10-ethano-anthracene-11,12-dicarboxylic acid 4

The cream solid was recrystallized from DMF, m.p. 275–276°C (75% yield) [7].

IR spectrum (KBr, cm^{-1}): 570 m, 745 m, 760 w, 920 w, 1020 m, 1220 w, 1250 w, 1350 w, 1470 w, 1515 m, 1600 s, 1640 $vs_{(C=O)}$, 2900–3050 m, 3320 vs_{NH}, 3350 s_{NH}.

Dipyrazole 5

A white solid was obtained by trituration with diethyl ether (m.p. 233–4°C).

Elemental analysis found (calculated): C 73.05% (74.67%), H 5.64% (5.78%), N 11.39% (12.44%).

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Table 1 ^{1}H NMR spectra of dibenzobicyclo[2.2.2]octane derivatives

Compound	Solvent	Aromatic region	Bridge	Bridgehead	Others
Ester **3**	CDCl$_3$	7.32 m H$_1$,H$_5$; 7.24 m H$_4$,H$_8$; 7.11 m H$_3$,H$_7$;7.18 m H$_2$,H$_8$	3.42 s H$_{11}$,H$_{12}$	4.72 s H$_9$,H$_{10}$	3.62 s CH$_3$
Hydrazide **4**	DMSO	7.29 m H$_1$,H$_5$; 7.16 m H$_4$,H$_8$; 7.07 m H$_3$,H$_7$; 7.03 m H$_2$,H$_6$	3.10 s H$_{11}$,H$_{12}$	4.50 s H$_9$,H$_{10}$	3.75 NH
Pyrazole **5**	CDCl$_3$	7.38 m H$_1$,H$_5$; 7.28 m H$_4$,H$_8$; 7.14 m H$_3$,H$_7$; 7.11 m H$_2$,H$_6$	4.47 s H$_{11}$,H$_{12}$	4.78 s H$_9$,H$_{10}$	5.86 s CH 2.42 s CH$_3$ 2.00 s CH$_3$

IR spectrum (CCl$_4$, cm^{-1}): 701 w, 755 s, 768 m, 913 w, 939 w, 963 m, 1248 w, 1325 vs, 1342 s, 1381 vs, 1410 m, 1582 m, 1720 vs$_{(C=O)}$, 2907 w, 2971 w, 3024 w, 3070 w, 3101 w.

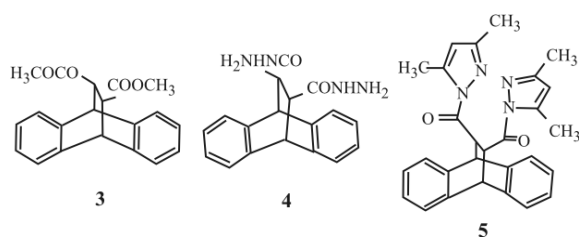^{13}C NMR Spectrum (CDCl$_3$, ppm): 172.61 (C=O), 151.34 (C=N), 144.0 (C–N), 142.48 (C$_{8a}$); 140.81 (C$_{4a}$); 126.19 (C$_2$,C$_6$); 126.05 (C$_3$,C$_7$); 125.44 (C$_4$,C$_8$); 123.51 (C$_1$,C$_5$); 52.32 (CH$_3$); 48.87 (C$_9$,C$_{10}$); 46.92 (C$_{11}$,C$_{12}$), 14.47 (CH$_3$), 13.45 (CH$_3$).

Thermal analysis of the compounds 3–5

The thermal decomposition of the compounds was followed with thermal balance TG 209 of Netzsch. Samples of 4–6 mg were placed in alumina crucible and heated with 10°C min^{-1} from room temperature to 800°C, under the flow of 10 mL min^{-1} dried N$_2$.

Results and discussion

New derivatives **3–5** having the same dibenzo[2.2.2]octane moiety have been synthesized and some of their coordination compounds have been prepared and their structures established based on spectral and elemental analysis data.

The synthesis of the dibenzobicyclic compounds started with a diene type reaction. Thus, from anthracene and fumaric ester by a diene reaction the polycyclic ester **3** has been obtained. The reaction takes place only in the presence of AlCl$_3$ in a ratio of 2:1 toward the reagents. According literature [8] the complex formed from fumaric ester and AlCl$_3$ has the reaction orbital (LUMO) energetically closer to that of anthracene HOMO orbital. As known before [9], a smaller difference between the diene partner orbital energies leads to a higher reactivity.

By the nucleophilic substitution of the ester groups the ester gave, on treatment with NH$_2$NH$_2$ hydrate as nucleophile, the $_{trans}$dihydrazide **4**.

Starting from the compound **4** the dipyrazole **5** has been obtained by treatment with diacetyl in acidic media, as previously described [4]. The spectral data as well as the elemental analysis are in agreement with the proposed structure. The behaviour of such compounds as ligands is of interest [10, 11].

The structures of the synthesized compounds were confirmed by the spectral measurements IR (Experimental) and NMR spectra. The ^{1}H NMR data are presented in Table 1. As expected, the different functional groups, placed in position 11 and 12 influenced the values of the chemical shifts for bridge and bridgehead protons.

The bridge and the bridgehead protons are deshielded in the case of dipyrazole **5**, due to the carbonyl groups, the higher effect being noticed for the bridge protons.
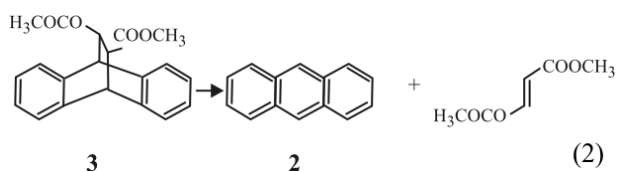
The thermal analysis of the compound **3–5** gave information about these compounds stability and suggested a decomposition pathway. The TG curves follow the mass decrease with the linear increase in temperature.
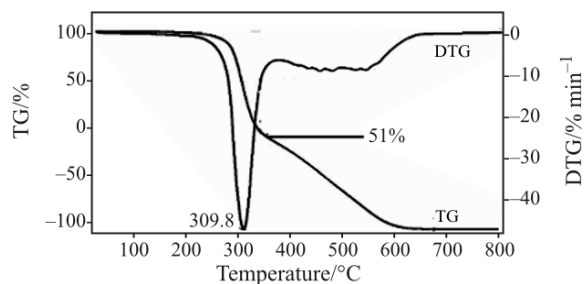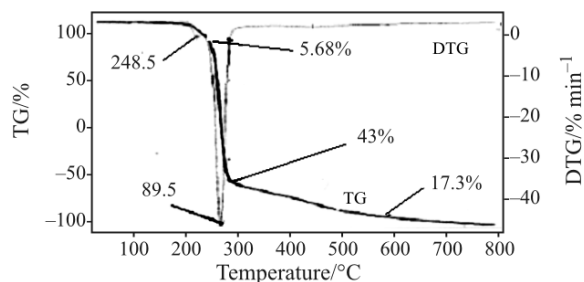
The ester **3** decomposed at 309.8°C (Fig. 1).

According the experimental mass loss (51%) a retrodiene reaction (2) with anthracene elimination (55% mass loss) being plausible, like in the case of the hydroxy-aldehyde **1** [5].
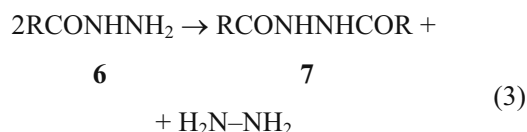
The dihydrazide **4** transformations followed a general pattern. The experimental results are shown in Fig. 2.

According the literature data concerning hydrazide thermal behaviour, a monoacylhydrazine **6**
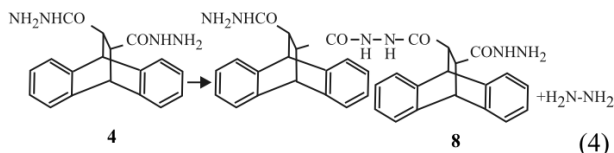

(2)

Fig. 1 Thermal behaviour of ester **3**

Fig. 2 Thermal behaviour of dihydrazide **4**

eliminates in the first step a molecule of hydrazine (3) leading to a diacyl hydrazine **7** [12].

$$2RCONHNH_2 \rightarrow RCONHNHCOR +$$

$$\mathbf{6} \qquad\qquad \mathbf{7}$$
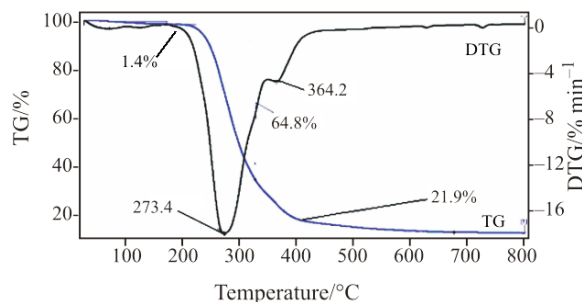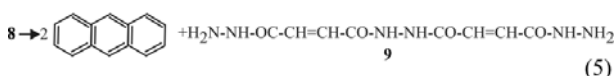
$$+ H_2N–NH_2 \qquad\qquad (3)$$

Such transformation was observed also in the case of dihydrazide **4** with an elimination of 1/2 mole of hydrazine/mole of hydrazide (5.68% experimental mass loss *vs.* 5% calculated mass loss) with the formation of compound **8**.

The next step in the decomposition of the new formed compound is, most probably, a retrodiene reaction with anthracene elimination (43% calculated mass loss *vs.* 45.9% the calculated value) and formation of the unsaturated polyhydrazide **9**.
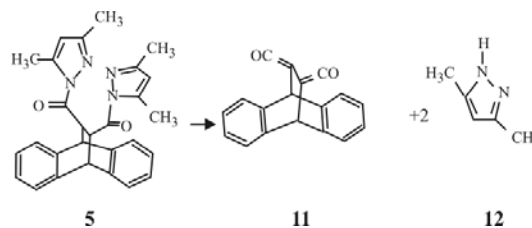

$$(4)$$

Elimination of the diketene **10** (O=C=C=C=O) fragments from the polymer **9** is in agreement with the next mass loss (experimental 21.5 % *vs.* calculated 18%).

$$(5)$$

Fig. 3 Thermal behaviour of dipyrazole **5**

The dipyrazole **5** thermal decomposition is determined by the presence of the pyrazole moiety as shown by the Fig. 3.

Thus, an elimination of the dibenzo[2.2.2]octane moiety as a dibenzobicyclo[2.2.2]octane diketene **11** happens.

Such behaviour was observed in other pyrazolone decompositions [10, 11, 13, 14]. A similar degradation was evidenced in the synthesis of the copper coordination compound of dipyrazole **5** [unpublished results].

Conclusions

The thermal behaviour of dibenzobicyclo[2.2.2]octane derivatives depends on the bridge substituents. The most stable is the ester **3** which decomposes starting with 309.8°C. The next in line is the dipyrazole **5** (273.4°C) followed by the dihydrazide **4**, which starts to decompose at 248.5°C.

The ester **3** and the dihydrazide **4** have the same pattern of thermal behaviour implying a retrodiene reaction.

The presence of the pyrazole moieties changed the general behaviour due, most probably to the stability of these aromatic parts. In this case the dibenzo[2.2.2]octane moiety leaves as diketene.

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