

*Dedicated to the memory of  
Professor Mircea D. Banciu (1941–2005)*

## MASS SPECTRUM FRAGMENTATION OF 10,11-DIHYDRO-5H-DIBENZO[*a,d*]CYCLOHEPTEN-5-ONE

Michaela Dina STĂNESCU,<sup>a\*</sup> Nicolae DINCĂ<sup>a</sup> and Eugen ŞIŞU<sup>b</sup>

<sup>a</sup>“Aurel Vlaicu” University, Faculty of Food Engineering, Tourism and Environmental protection, Bd. Revoluţiei 77,  
310130 Arad, Roumania, Fax 0040257280070

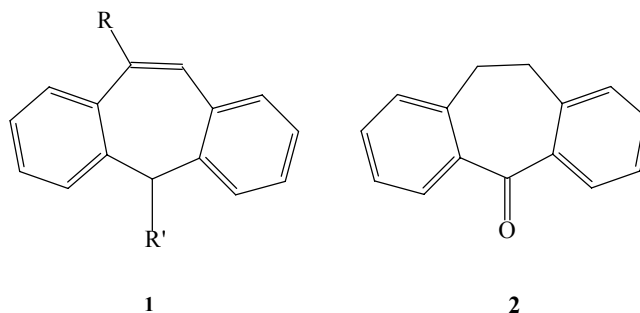
<sup>b</sup>“Victor Babeş” University of Medicine and Pharmacy, Faculty of Pharmacy, Piata Eftimie Murgu nr. 2,  
300041 Timișoara, Roumania

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The dibenzo[*a,d*]cycloheptene skeleton is of importance taking into account the presence of this moiety in different compounds having theoretical or practical interest. A key intermediate in the synthesis of such compounds is 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-one. The study of the MS fragmentation of this ketone may give information about the possible fragmentation of similar compounds. The central seven-member ring leads to a different MS fragmentation pattern, compared with the simple dibenzylic ketone (benzophenone). The formation energy ( $\Delta H_f$ ) of the molecules and ions resulted during fragmentation have been calculated by the semi-empirical methods AM1, using the package of programmes HyperChem 5.11.

### INTRODUCTION

A large number of substituted dibenzo[*a,d*]cycloheptenes (**1**) have been intensely studied by Nenitzescu, Cioranescu, Banciu and co-workers. Partial reviews<sup>1,2</sup> presented these researches. The compounds having such skeleton are of interest for theoretical and practical aspects.<sup>3</sup> Their synthesis has generally as a key compound, the 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-one (**2**). Thus, the properties of ketone **2** seem worthwhile to be studied.

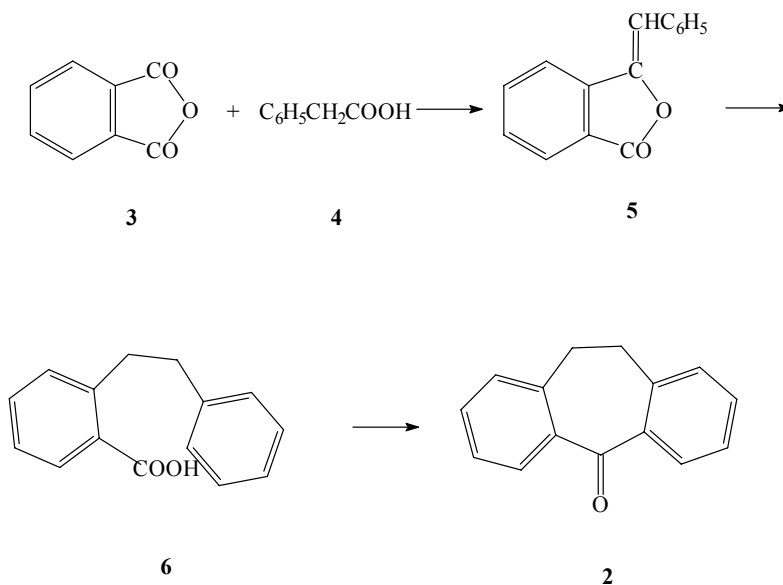


This paper presents the mass spectrum of the compound **2** proposing structures for the obtained fragments. As previously described,<sup>4,5</sup> connections between the chemical behaviour and the mass spectra have been observed, for polycyclic compounds having a similar skeleton.

\*Corresponding author, E-mail: stanescu@uav.ro

## RESULTS AND DISCUSSION

The ketone **2** was synthesized, by the method previously described,<sup>6</sup> starting from phthalic anhydride (**3**) and phenylacetic acid (**4**) through the following steps:



The mass-spectrum data are presented in Table 1.

Table 1

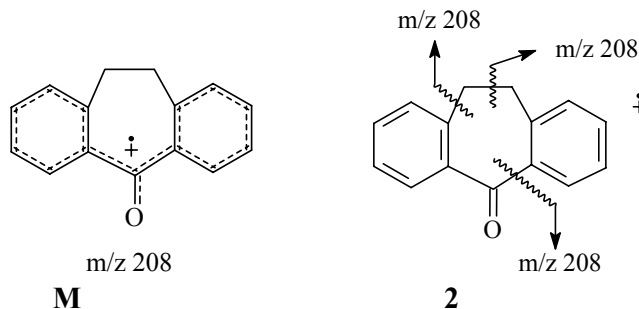
Mass spectrum of 10,11-Dihydro-5H-dibenzo[*a,d*]cyclohepten-5-one

No	<i>m/z</i>	%BP	No	<i>m/z</i>	%BP	No	<i>m/z</i>	%BP
1.	<b>210 (M+2)</b>	1.3	19.	<b>163</b>	2.0	37.	<b>99</b>	0.7
2.	<b>209 (M+1)</b>	16.1	20.	<b>153</b>	3.1	38.	<b>98</b>	1.1
3.	<b>208 (M)</b>	100	21.	<b>152</b>	13.6	39.	<b>90</b>	7.8
4.	<b>207 (M-1)</b>	36.7	22.	<b>151</b>	6.9	40.	<b>89</b>	21.5
5.	<b>205 (M-3)</b>	0.8	23.	<b>150</b>	3.5	41.	<b>87</b>	1.9
6.	<b>194</b>	1.1	24.	<b>139</b>	3.0	42.	<b>86</b>	1.3
7.	<b>193</b>	7.8	25.	<b>131</b>	2.0	43.	<b>82</b>	2.1
8.	<b>191</b>	1.4	26.	<b>130</b>	1.4	44.	<b>78</b>	1.3
9.	<b>189</b>	0.9	27.	<b>128</b>	1.4	45.	<b>77</b>	6.5
10.	<b>182</b>	0.8	28.	<b>127</b>	1.2	46.	<b>76</b>	10.8
11.	<b>181</b>	9.0	29.	<b>126</b>	1.8	47.	<b>75</b>	3.6
12.	<b>180</b>	63.8	30.	<b>115</b>	2.6	48.	<b>74</b>	2.8
13.	<b>179</b>	62.9	31.	<b>113</b>	0.8	49.	<b>65</b>	1.5
14.	<b>178</b>	48.1	32.	<b>105</b>	1.1	50.	<b>64</b>	2.2
15.	<b>176</b>	11.5	33.	<b>104</b>	1.0	51.	<b>63</b>	7.9
16.	<b>174</b>	0.8	34.	<b>103</b>	3.9	52.	<b>62</b>	2.3
17.	<b>166</b>	4.6	35.	<b>102</b>	2.7	53.	<b>52</b>	0.9
18.	<b>165</b>	32.3	36.	<b>101</b>	0.9	54.	<b>51</b>	5.1

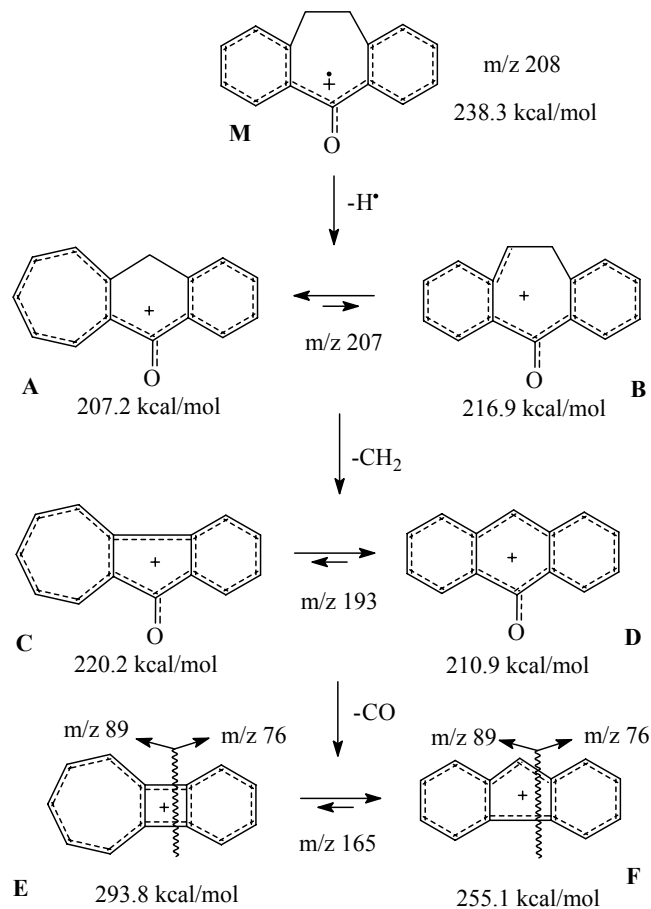
The geometries of the proposed fragments have been optimised with the field of forces MM+ and re-optimised with the semi empirical method AM1,<sup>7</sup> using the operators RHF for molecules or ions and UHF for the radical ions. The convergence limit SCF was  $10^{-5}$ , using the accelerated convergence procedure. For the optimisation of the geometries the conjugated gradient method – Polak-Ribiere has been used, with a gradient  $RMS = 10^{-2}$ , the structures being considered in vacuum. The heat of formation ( $\Delta H_f$ ) of the molecules and ions obtained by fragmentation was calculated based on the package of programmes HyperChem 5.11.<sup>8</sup> It is worthwhile mentioning that this method has been applied with success for similar structures.<sup>9</sup>

The molecular peak **M** ( $M=208$ ) is very stable (even at 70 eV) being the base peak (BP), due to the extended conjugation, as well as to the capacity of the molecule to take energy without changing the structure (relaxation energy). The relative intensity of the fragments 209 ( $M+1$ ) and 210 ( $M+2$ ) are in

agreement with the values expected from the isotopic distribution. The fragmentation evidenced for the unbridged benzyl ketone (Benzophenone) leading to the BP with  $M=105$ , corresponding to the fragment  $C_6H_5CO$ ,<sup>10</sup> is no more possible for the ketone **2**, due to the presence of the central ring. The seven-member ring changed the behaviour of the molecule by stabilizing the tricyclic fragments *versus* the fragments that would result by the cleavage of the central ring.

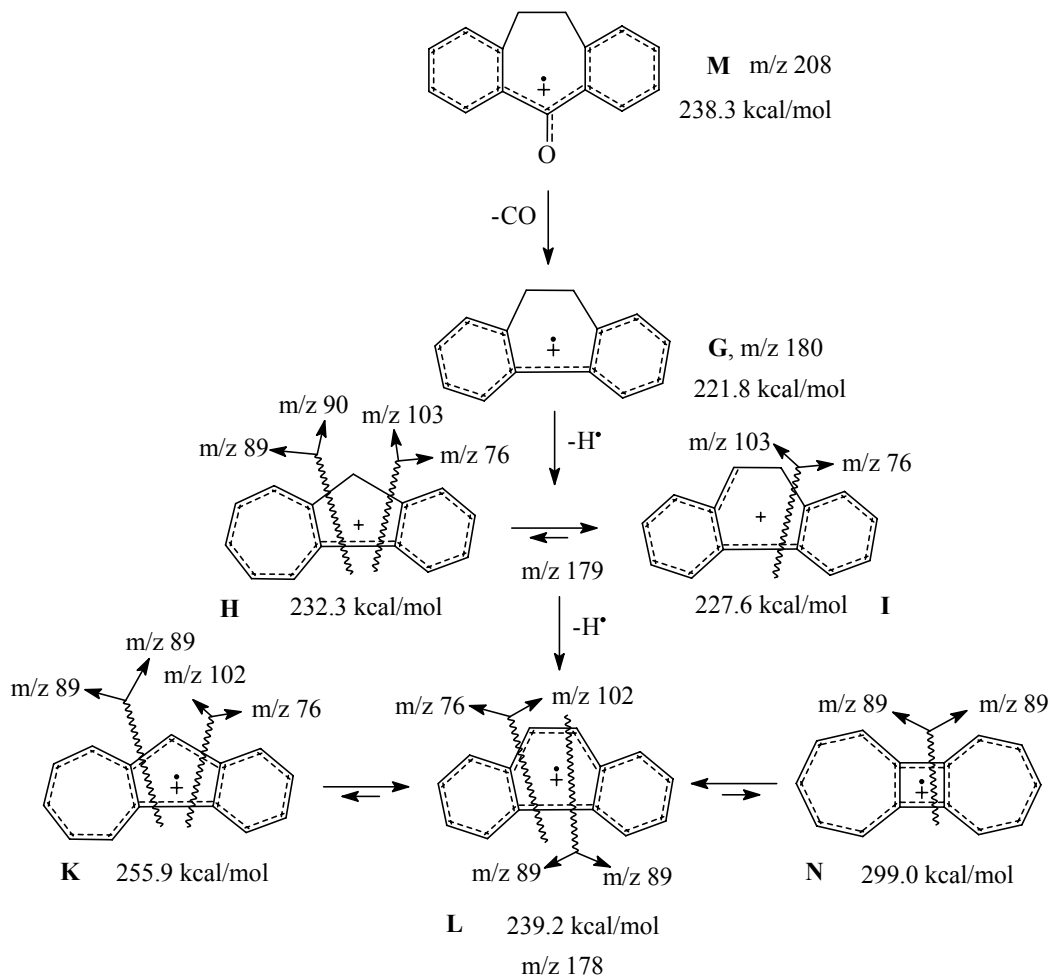


As expected, the stability of the structures obtained by benzylic hydrogen elimination makes this transformation the main route in the compound **2** fragmentation (see **Scheme 1**) leading to the ions **A** (**B**) ( $M=207$ ; 36.7 % BP). By elimination of a  $CH_2$  group the polycyclic system **B** is transformed into an anthracene skeleton **D** ( $M=193$ ; 7.8%) stabilized by extended conjugation. From the ion **A** by a similar fragmentation the polycyclic structure **C** may be obtained. A further CO moiety elimination generated the ion of fluorene (**F**), also very stable, or the structure **E** ( $M=165$ ; 32.3 %).



Scheme 1

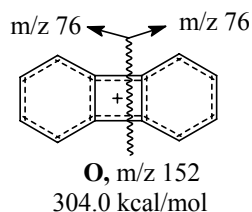
The fragments  $M=180$ , 179, 178 (see **Scheme 2**) could be explained by an elimination of the CO molecule with the formation of dihydro-phenanthrene radical-ion **G** ( $M=180$ ; 63.8 %). By benzylic hydrogen eliminations the structures **I/H** ( $M=179$ ; 62.9 %) and the phenanthrene ion **L** ( $M=178$ ; 48.1 % BP) were generated. For all these fragments there are peaks corresponding to  $M+1$  and  $M+2$  superposed on the corresponding neighbour fragments.



Scheme 2

The higher abundance of fragments 180,179,178 compared with the fragment 193 attests the fact that CO elimination is of preponderance compared with a  $\text{CH}_2$  fragmentation. In fact, the same fragments could be obtained by a breaking of the  $\text{CH}_2\text{-CH}_2$  bridge with formation of a diradical which gives, after a number of rearrangements, the 9,10-dihydroanthracene **G'** structure ( $M=180$ ).<sup>11</sup> By successive benzylic hydrogen elimination from this fragment, the fragments  $M=179$  and  $M=178$  (anthracene) may be obtained.

A  $\text{CH}_2$  elimination from the most stable species **L** gave the biphenylene ion **O** ( $M=152$ ; 13.6 % BP) that is also very stable due to the extended conjugation.



The smaller fragments 89 and 76 could be obtained by further fragmentation of the polycyclic structures with formation of a C<sub>7</sub> or C<sub>6</sub> radical-ions as previously evidenced<sup>4,5</sup> for similar structures.

As expected, the fragmentation of the molecular ion **2a** leads to tricycle structures. This assertion is in agreement with the values of the heat of formation corresponding to these ions, which are smaller compared with those calculated for the possible ions with di- or mono-cyclic structures. Except ion **A** the dibenzo-annulated structures seem to be preferred to those having C<sub>7</sub> cycle taking in account the calculated values for the formation energy ( $\Delta H_f$ ). The chemistry of the studied compound is developing in the same way, with conservation of the polycyclic structures.<sup>12</sup>

## CONCLUSIONS

All the processes were developed to the formation of the most stable fragments.

The polycyclic structure was preserved during fragmentation due to the stability of such structures, explained by extended conjugation.

The calculation of the  $\Delta H_f$  help to understand the fragmentation process and to propose the intermediate structures formed during this process. Benzoannulated structures are preferred according the  $\Delta H_f$  values.

## EXPERIMENTAL

**3-Benzylideneophthalide (5)** was synthesized according literature<sup>6a</sup> by the condensation of phthalic anhydride (**3**) and phenyl acetic acid (**4**) at 230-240°C, 6 h. From the cooled mixture dissolved in ethylic alcohol, a yellow solid was isolated by filtration (m.p. 97°C, yield 80-85 %). IR Spectrum (CHCl<sub>3</sub>, cm<sup>-1</sup>): 860w, 900w, 970s, 1070s, 1260m, 1340m, 1450w, 1465w, 1480w, 1600w, 1760vs (C=O), 2890w, 2940w, 3010w.

**2-Phenylethylbenzoic acid (6)** obtained from the compound **5** by treatment with HI<sup>6b</sup> (57 %) and red P, at reflux for 6 h, according Campbell and co-workers<sup>6b</sup> is a white solid [m.p. 130-131°C(acetone), yield 75-80 %]. IR Spectrum (CHCl<sub>3</sub>, cm<sup>-1</sup>): 1060m, 1070m, 1120m, 1250s, 1280s, 1370m, 1440m, 1480m, 1680vs (C=O), 2300-3100 large.

**10,11-Dihydro-5H-dibenzo[a,d]cyclohepten-5-one (2)** was prepared by cyclization of acid **6** with polyphosphoric acid<sup>6c</sup> by heating for 2-3 h, with stirring, at 170-180°C. After the usual work up a yellow compound was isolated by vacuum distillation (m.p. 42°C, yield 75-80 %). IR Spectrum (CHCl<sub>3</sub>, cm<sup>-1</sup>): 919i, 938i, 952i, 1100w, 1149m, 1241m, 1291vs, 1350w, 1449s, 1460w, 1597m, 1648 vs (C=O), 2859w, 2920w, 2945w, 3025w and 3070w. <sup>1</sup>H-NMR Spectrum (CDCl<sub>3</sub>, ppm): 3.2 (s, 4H, H<sub>10,11</sub>), 7.2-7.5 (m, 6H, H<sub>arom.</sub>), 8.0-8.1 (dd, 2H, H<sub>arom.</sub>).

The MS was recorded using a GC Hewlett Packard 5890 with Detector MSD 5972, operating at EI 70eV, column HP-5M5, carrier gas He (5ml/min), temperature injector 180°C, with a probe temperature range between 50-250°C.

The heats of formation ( $\Delta H_f$ ) of the molecules and ions obtained by fragmentation have been calculated according the semi empirical methods AM1,<sup>7</sup> using the package of programmes HyperChem 5.11.<sup>8</sup>

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