

Electron Impact and Ammonia Chemical Ionization Mass Spectra of *n*-Azabicyclo[*m*.2.0]alkan-(*n* + 1)-ones (*m* = 3-6, *n* = 6-9)

Kalevi Pihlaja†

Laboratory for Physical Chemistry, University of Turku, SF-20500 Turku 50, Finland

Pirjo Vainiotalo

Department of Chemistry, University of Joensuu, SF-80101 Joensuu 10, Finland

Gábor Bernáth

Institute of Pharmaceutical Chemistry, University Medical School, POB 121, H-6701 Szeged, Hungary

György Göndös and Lajos Gera

Institute of Organic Chemistry, József Attila University, Dóm Tér 8, H-6720 Szeged, Hungary

Electron impact induced fragmentation of the title compounds obeys a route where the lactam moiety, OCNH, is cleaved first, with the accompanying formation of a cycloalkene ion. This can be verified by low-resolution, high-resolution, *B/E* and *B²/E* spectra as well as by collisional activation spectra of, for example, the ions *m/z* 82 and 67 from 7-azabicyclo[4.2.0]octan-8-one and from cyclohexene. The only, and fairly weak, fragment ions including O and N are [C₃H₃O]⁺, [C_{*k*}H_{2*k*-2}N]⁺ (*k* = 5-8) and [C₃H₆N]⁺. The ammonia chemical ionization spectra are also characteristic for all four lactams and show the same dominant ions in all cases, namely [M + 1]⁺, [M + 1 + NH₃]⁺ and [2M + 1]⁺.

In the context of our studies on condensed skeleton azetidines¹ their corresponding azetidones (1-4) were also synthesized. Their mass spectra were recorded and found to be very interesting. Since no mention of them could be found in the literature we decided to report our findings as follows.

EXPERIMENTAL

Synthesis of the azetidones 1-4

6-Azabicyclo[3.2.0]heptan-7-one (1), 7-azabicyclo[4.2.0]octan-8-one (2), 8-azabicyclo[5.2.0]nonan-9-one (3) and 9-azabicyclo[6.2.0]decan-10-one (4) were prepared by a modified method of Bestian *et al.*² where carefully dried cycloalkene (0.5 mol) was allowed to react with chlorosulphonyl isocyanate (0.5 mol) in dichloromethane at reflux temperature for 24 h. The dark-brown reaction mixture was diluted with 50 cm³ of Et₂O and added then dropwise to 25 cm³ of an aqueous solution including 1.5 g of KI and 2.5 g of KH₂PO₄. The resulting mixture was cooled down to 273 K and saponified by adding dropwise 5M NaOH and vigorously stirring while the pH was kept between 3 and 5 (glass electrode). After the saponification reaction the PH was adjusted to

neutral level. Finally the solution was extracted with 5 × 100 cm³ of dichloromethane (in the case of 3 with the same amount of trichloromethane). Before evaporating the solvent the extract was dried overnight on anhydrous Na₂SO₄. The crude products were purified by distillation under reduced pressure (3 mm Hg). The above method gave compounds 1, 2 and 4 in 15-18% better yields than the original literature method.² 3 (m.p. 329 K) had not been previously prepared. The sample of 7-azabicyclo[4.2.0]-4-octen-8-one³ was kindly donated by Dr Gera.

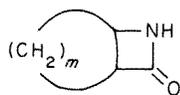
Mass spectra

The 15 and 70 eV low-resolution (*R* = 500) and the 70 eV high-resolution (*R* = 5000) electron impact (EI) as well as the ammonia chemical ionization (NH₃CI) spectra (at 8 × 10⁻⁶ Torr) were recorded on a Jeol JMS-D300 mass spectrometer equipped with the JMA-3500 data system. The accelerating voltage was 3 kV, the temperature of the ion source 343 K and the ionization current 300 μA. The direct inlet probe was kept at ambient temperature (~300 K). Linked scans were recorded both at constant *B/E* and *B²/E* using the above conditions with the exception of the nominal resolution which was now 1000. In some cases the collisional activation (CA) spectra with He at 30% transmission level were utilized to clarify further the major fragmentation pathways.

† Author to whom correspondence should be addressed.

RESULTS AND DISCUSSION

The major ions of the 70 eV EI spectra of 1–4 are shown in Table 1 and those of the 70 eV NH₃CI spectra in Table 3. Table 2 compares the He CA spectra of the molecular and [M–15]⁺ ions of cyclohexene (*m/z* 82 and 67, respectively) with those of the corresponding ions from 7-azabicyclo[4.2.0]octan-8-one (2).



- 1: *m* = 3
 2: *m* = 4
 3: *m* = 5
 4: *m* = 6

All of the EI spectra show a weak [M + 1]⁺ ion which is, however, more intense than the [M]⁺ ion itself. This is due to the relatively high volatilities of

Table 1. The predominant ions and their relative abundances in the mass spectra of 1–4

ion	<i>m/z</i>	Compound (rel. abund.)			
		1	2	3	4
C ₉ H ₁₆ NO	154				1.5
C ₉ H ₁₅ NO	153				0.4
C ₉ H ₁₄ NO	140			2.6	
C ₈ H ₁₃ NO	139			0.3	
C ₇ H ₁₂ NO	126		0.8		
C ₇ H ₁₁ NO	125		0.1		
C ₈ H ₁₄ N	124				0.2
C ₆ H ₁₀ NO	112	0.7			
C ₇ H ₁₃ N	112			0.4	
C ₆ H ₉ NO	111	0.4			
C ₇ H ₁₂ N	110			0.7	
C ₈ H ₁₄	110				76.8
C ₆ H ₁₁ N	97		0.2		
C ₆ H ₁₀ N	96		0.5		
C ₇ H ₁₂	96			95.5	
C ₇ H ₁₁	95			6.4	23.4
C ₅ H ₉ N	83	0.8			
C ₅ H ₈ N	82	2.9			
C ₆ H ₁₀	82		74.4		100
C ₆ H ₉	81		8.6	100	55.2
C ₆ H ₈	80				5.6
C ₆ H ₇	79		4.0	6.6	7.2
C ₆ H ₅	77		1.9	3.0	2.7
C ₄ H ₇ N	69		2.3		
C ₅ H ₉	69				15.0
C ₅ H ₈	68	100		65.7	39.9
C ₅ H ₇	67	85.9	100	97.2	95.2
C ₅ H ₆	66	4.0	1.8	10.0	
C ₅ H ₅	65	2.8	1.8	3.5	
C ₃ H ₆ N	56	4.6	2.8	9.4	6.2
C ₄ H ₈	56				6.2
C ₃ H ₃ O	55	6.2	3.5	7.1	6.0
C ₄ H ₇	55			40.0	16.7
C ₃ H ₄ N	54	4.6			
C ₄ H ₆	54		63.0	83.4	66.9
C ₄ H ₅	53	10.4	5.2	11.2	10.7
C ₃ H ₅	41	9.8	22.1	25.0	43.8
C ₃ H ₃	39	10.4	14.3	23.9	22.1

Table 2. The He CA spectra of ions *m/z* 82 and 67 from cyclohexene and 2

<i>m/z</i>	Precursor <i>m/z</i> 82 from		<i>m/z</i>	Precursor <i>m/z</i> 67 from	
	2	Cyclohexene		2	Cyclohexene
26	1.7	1.9	26	3.3	3.1
27	8.6	8.2	27	7.8	7.5
28	2.4	2.2	28	0.9	0.3
29	1.5	1.4	37	3.7	3.1
37	—	0.3	38	6.3	6.1
38	1.8	1.6	39	29.1	28.3
39	13.7	14.5	40	6.5	6.3
40	2.0	1.9	41	21.9	24.0
41	13.4	12.8	50	2.0	2.0
42	0.4	—	51	2.8	3.1
50	1.5	1.8	62	0.5	—
51	2.5	3.0	63	2.9	2.5
52	1.8	2.0	65	12.3	13.6
53	7.2	7.2			
54	20.9	19.6			
55	1.8	1.7			
65	2.0	2.0			
66	2.8	2.4			
77	3.4	3.6			
79	7.7	8.8			
80	2.9	3.2			

the compounds studied which leads to a 'self-CI' process in the ion source. By introducing lactam 1 through a liquid inlet system to decrease its evaporation appreciably the [M + 1]⁺ ion could still be seen but it was clearly less intense than the [M]⁺ ion.

The main fragmentation (a, Scheme 1) is always initiated by the loss of the lactam moiety, OCNH, and a cycloalkene ion, C_{*n*}H_{2*n*-2} (*n* = 5–8), is obtained. This can be verified by comparing the sub-spectra resulting from these ions with the library spectra of the respective cycloalkenes.⁴⁻⁶

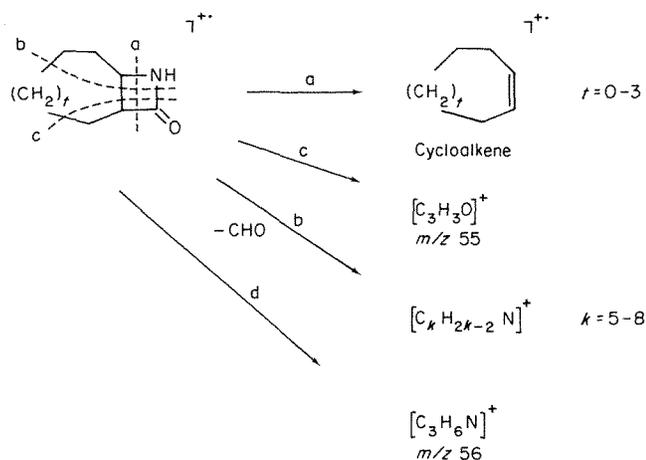
In the case of 7-azabicyclo[4.2.0]octan-8-one (2) this was also confirmed by comparing the He CA spectra of its ions *m/z* 82 and 67 with those of [M]⁺ (*m/z* 82) and [M – 15]⁺ (*m/z* 67) of cyclohexene itself (Table 2).

Parallel to the predominant formation of the cycloalkene ions weak ions corresponding to the loss of CHO can also be seen (b, Scheme 1). The latter are, however, due to a high-energy process which cannot be observed at all at low ionizing energies (≤ 15 eV). At 15 eV only the [M + 1]⁺ and cycloalkene ions and a few other hydrocarbon fragments (if any) can be seen in the spectra of 1–4.

A third primary process (c, Scheme 1) which begins from the molecular (or [M + 1]⁺) ions is the formation of the [C₃H₃O]⁺ (*m/z* 55) ions (Table 1) which is also

Table 3. The relative abundances of the main peaks in the NH₃CI spectra of 1–4

Compound	[M + H] ⁺	[M + H + NH ₃] ⁺	[2M + H] ⁺
1	82.9	100	12.4
2	51.7	100	11.2
3	66.0	100	12.1
4	64.0	100	2.7



a high-energy route in comparison with a. The ion C_3H_6N (m/z 56) can be seen in all of the 70 eV spectra (Table 1) and according to the metastable studies and CA spectra it is also formed from the molecular (or $[M+1]^+$) ions (route d) rather than via the $[C_kH_{2k-2}N]^+$ ions.

For comparison the 70 eV EI spectrum of 7-azabicyclo[4.2.0]-4-octen-8-one was also recorded. The major primary product is 1,3-cyclohexadiene in agreement with the mechanism found for the saturated counterparts above.

The NH_3CI spectra are characteristic for all the lactams 1-4. The base peak is always given by the ammonia adduct of the $[M+H]^+$ ion, which is also very intense (Table 3). Surprisingly, the peak corresponding to the protonated dimer is fairly intense ($\sim 12\%$) in all but 4 ($\sim 3\%$) where the size of the adduct has obviously exceeded the critical level.

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