A mass spectrometric investigation on some 5-substituted adamantan-2-ones

Roberto Martínez, Raúl Cetina, Federico Jiménez, Luis Velasco and Javier Pérez
Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, México

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Abstract. The mass spectrometric behavior of a series of 5-substituted adamantan-2-ones has been studied in different ionization conditions (Electron Ionization and Fast Atom Bombardment), with the aid of linked scan experiments.

1. Introduction

It is well known that torsional and electrostatic effects are important in determining facial selectivity in reactions of aldehydes and ketones [1–4]. 5-substituted adamantanone derivatives are compounds that have been used to study electronic effects in diastereoselectivity [5,6], because their structures are an ideal substrate to investigate electronic effects in transition state energy since both faces of the carbonyl are little affected by steric effects of substitution at C5 [7–9]. In spite of this, the mass spectrometry of 2-adamantanone 5-substituted derivatives has hitherto not been investigated. This observation prompted us to prepare also some simpler compounds of this type and to investigate systematically their mass spectrometric behavior.

2. Experimental

The 5-substituted adamantan-2-ones were synthesized according to the described procedures [10–16]. Low resolution mass spectra were recorded using a Jeol JMS-AX 505 HA mass spectrometer using the direct inlet system with an ionization energy of 70 eV, an emission current of 100 μ A and ion source temperature of 150°C. Measurements of exact mass were performed on a Jeol JMS-SX 102A mass spectrometer at a resolution of 10,000 using perfluorokerosene (PFK) as an internal reference. The differences between measured and theoretical values were less than 5 ppm. Daughter ions were recorded on the same instrument using the linked scan mode. Fast Atom Bombardment mass spectra were obtained bombarding nba-acetone solutions with 6 keV Xenon atoms [17].

Scheme 1. R=H, OH, OMe, OAc, F, Cl, Br, I, CO₂Me, Ph.

Scheme 2.

3. Results and discussion

The fragmentation and the specific degradations proposed for 5-substituted 2-adamantanones are depicted in schemes 2–6. The key ions and their relative abundance observed in the electron impact (EI) mass spectra of compounds **1**–**10** are compiled in Table 1. The elemental compositions of the key ions were determined by exact mass measurements.

The 5-substituted 2-adamantanones are relatively stable under electron impact, except compound **8**, and the compounds **1**, **5**, **6**, **9** and **10** show the molecular ion **a** as a base peak. The fission of the molecular ion **a** is initiated by the familiar α -cleavage of ketones, which has been shown [18–21] to produce the most abundant fragments arising from the parent ion. In the present case, α -fission at the C2–C3 bond is attended, possibly in a concerted process, together with simultaneous hydrogen migration to C2, leading to the central intermediate **b** (Scheme 2). This ion eliminated the 5-substituent by β -fission to C3=C4 double bond, yielding the species **c** at m/z [M–R], the base peak of compounds **7** and **8**; however this loss is completely absent in the fragmentation of **1**, **3**, and **5** analogs. This behavior may be rationalized in terms of leaving capability of the 5-R group.

The spectra further reveal the loss of water from the ion **c** to give the ion at m/z [M–R–H₂O], **d**. The nature of these dehydrations, which are known to proceed by a complex mechanism involving rearrangements even in simple alicyclic molecules remains unresolved [22]. The examination of 2-adamantanone incorporating deuterium in specified positions may not provide entirely decisive

Scheme 3.

Scheme 4.

Table 1
Key ions in the EI mass spectra of 5-substituted adamantan-2-ones (**1–10**)

Compound	R	M+•	M-R	M-R-H ₂ O	M-R-CO	M-H ₂ O	M-CO	[78-R] ⁺
		a, b	c	d	e	f	g	h
1	H	100.0	*	*	2.3	6.1	3.34	50.9
2	OH	61.3	2.7	*	3.9	16.0	5.6	100.0
3	OMe	49.5	*	*	*	*	6.3	100.0
4	OAc	11.8	3.7	*	12.2	*	12.3	
5	F	100.0	*	*	*	6.2	7.1	67.5
6	Cl	100.0	10.7	23.6	11.8	*	2.84	18.6
7	Br	34.9	100.0	6.6	67.1	*	*	*
8	I	2.0	100.0	2.7	32.6	*	*	*
9	COOMe	100.0	55.0	10.6	30.4	*	78.2	42.4
10	Ph	100.0	*	*	*	4.6	2.0	76.6

* Relative abundance less than 2%.

evidence, since extensive ‘scrambling’ of hydrogen and deuterium occurred under the operating conditions of the mass spectrometer [23]. In this case, it may propose the migration of one hydrogen from C8 and another from C9 to the carbonyl-oxygen; posterior, possibly in a concerted process, simultaneous fission of C2–C3 bond and elimination of one molecule of H₂O gives the ion **d** (Scheme 3). Likewise, the ion **c** loses carbon monoxide to yield the ion of $m/z [M - R - CO], e$ (Scheme 4).

Scheme 5.

Scheme 6.

Scheme 7.

It is interesting to note that relative abundance of the ions $m/z [M-R-H_2O]$ and $[M-R-CO]$ is high for compounds with $R=Cl, Br, I$ and $COOMe$.

The compounds analyzed, except **4**, **7** and **8**, also show a characteristic fragment at $m/z (78 + R)$ due to decomposition of bicyclic moiety of adamantan-2-one (Scheme 5). This ion is the base peak of compounds **2** and **3**. Finally, a typical expulsion of monoxide carbon and water from the molecular ions leads to the formation of the ions at $m/z [M-CO]$ and $m/z [M-H_2O]$, respectively. This degradation pattern was previously reported for 2-adamantanone [23]. The fragmentation mechanism may be similar to that depicted for the loss of CO and H_2O from $m/z [M-R]$ ion and it is described in Schemes 6 and 7.

The compounds examined ionized under FAB conditions showed similar mass spectral behavior as under EI conditions. However, as it is known, in positive ion FAB the most favored ionization process generally consists in a protonation reaction occurring in the selvedge region close to the solution [24]. By means of metastable ions studies (parent and daughter) and accurate mass measurements the common fragmentation pattern suggested by electron impact ionization was corroborated by linked scan on FAB spectrometry.

4. Conclusion

From mass spectral studies, some specific points can be underlined. First, the molecular ion intensity of all the compounds analyzed, except **8**, is strong. Second, the main fragmentation is determined by the 5-substituent on the 2-adamantanone moiety and by the 2-ketone group. The fragmentation pattern under FAB mass spectrometry of all the compounds studied is similar to the one under EI mass spectrometry and as it is well known, they give $[M + 1]$ strong ions.

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