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Electron Impact Mass Spectrometry of Substituted Benzyl(1-allylcycloalkyl)amines and Their Cyclization Products

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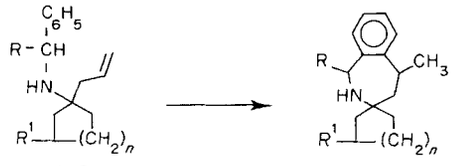
Electron impact mass spectra have been measured for benzyl(1-allylcycloalkyl)amines and α-phenylethyl(1-allylcycloalkyl)amines and for the spiro(benzo-2-azepine-3,1′-cycloalkanes) produced by their cyclization.

INTRODUCTION

In the course of synthetic research on new compounds with potential pharmacological activity, we have obtained intermediate benzyl-(**1**, **3**, **5**) and α-phenylethyl(1-allylcycloalkyl)amines (**2**, **4**, **6**) and the products of their cyclization, spiro(benzo-2-azepine-3,1′-cycloalkanes) (**1a–6a**). Because the mass spectra of both types of compounds were unknown, we undertook the study of their fragmentation under electron impact ionization.



1-6 Ia-6a

1 **1a** R = R¹ = H, *n* = 1
2 **2a** R = CH_3, R¹ = H, *n* = 1
3 **3a** R = R¹ = H, *n* = 2
4 **4a** R = CH_3, R¹ = H, *n* = 2
5 **5a** R = H, R¹ = CH_3, *n* = 2
6 **6a** R = R¹ = CH_3, *n* = 2

EXPERIMENTAL

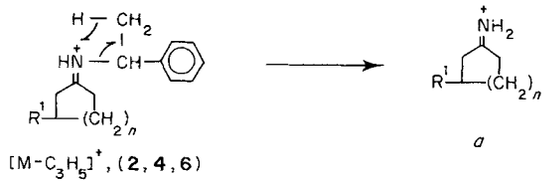
The compounds were analysed with a Kratos MS 25RF instrument with an electron energy of 70 eV and a source temperature of 220 °C. The direct inlet probe was heated from ambient temperature to 300 °C at 10 °C min^{-1}.

RESULTS AND DISCUSSION

Compounds **1–6** show unstable molecular ions. Their decomposition gives rise to two most abundant ions, $[M - C_3H_5]^+$ and $[C_6H_5CHR]^+$, which are due to competing 'amine' and 'benzylic' cleavages, respectively (Table 1). However, the base peaks for **1–6** are the ions $[C_6H_5CHR]^+$, which allow one to distinguish unambigously these compounds and isomeric structures **1a–6a**. Compounds **2**, **4** and **6** bearing a methyl substituent on the benzylic carbon atom show fragments (*a*) resulting from elimination of styrene from $[M - C_3H_5]^+$ ions (Scheme 1). For compounds **1**, **3**, **5** such a process is impossible.

Table 1. Characteristic ions in the mass spectra of benzyl(1-allylcycloalkyl)amines 1–6 (*m/z* (relative abundance, %))

Compound	$M^{+\cdot}$	$[M - C_3H_5]^+$	$[C_6H_5CHR]^+$	*a*
1	214 (8)	174 (85)	91 (100)	84 (1)
2	229 (6)	188 (51)	105 (100)	84 (55)
3	229 (6)	188 (66)	91 (100)	84 (1)
4	243 (2)	202 (44)	105 (100)	98 (92)
5	243 (13)	202 (92)	91 (100)	112 (1)
6	257 (1)	216 (87)	105 (100)	112 (95)



$[M-C_3H_5]^+$, (2, 4, 6) *a*

Scheme 1

For spiro(benzo-2-azepine-3,1′-cycloalkanes) (**1a–6a**) the intensities of the $M^{+\cdot}$ peaks increase sharply and constitute 30–50% of the base peaks (Table 2). Primary fragmentation of $M^{+\cdot}$ includes the loss of a CH_3 radical from the azepine ring and the cleavage of the carbocycle or heterocycle. It should be noted that a CH_3 radical can also be lost from some fragment ions retaining a methyl substituent.

The molecular ions of **1a–6a** decompose easily through cleavage of the cycloalkyl moiety, yielding the ions *b* and *c* (Scheme 2). Cleavage of the azepine ring gives rise to intense indane-type cation-radicals (*d*). Scission of the same bonds with charge localization on nitrogen accompanied by a hydrogen migration yields the ions *a* typical for **1–6**.

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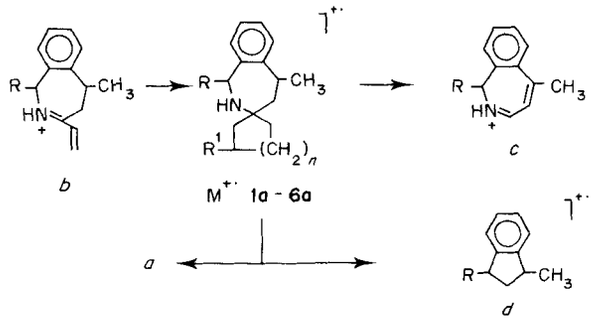

Scheme 2.

Table 2. Characteristic ions in the mass spectra of spiro(benzo-2-azepine-3,1′-cycloalkanes) 1a–6a (*m/z* (relative abundance, %))

Compound	$M^{+\cdot}$	$[M-CH_3]^+$	*a*	*b*	*c*	*d*	$[d-CH_3]^+$
1a	215 (42)	200 (90)	84 (33)	186 (100)	158 (23)	132 (61)	117 (78)
2a	229 (23)	214 (80)	84 (51)	200 (100)	172 (35)	146 (23)	131 (78)
3a	229 (47)	214 (30)	98 (51)	186 (100)	158 (12)	132 (60)	117 (50)
4a	243 (49)	228 (52)	98 (50)	200 (100)	172 (23)	146 (38)	131 (93)
5a	243 (25)	228 (20)	112 (20)	186 (100)	158 (12)	132 (62)	117 (48)
6a	257 (32)	242 (53)	112 (43)	200 (100)	172 (23)	146 (46)	131 (95)