# Mass Spectra of Bicyclo[2.2.1]-2-heptanols

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The fragmentation of bicyclo[2.2.1]-2-heptanol, endo- (I) and
exo- (Ia), 1-methylbicyclo[2.2.1]-2-heptanol, endo- (II) and exo-
(IIa) and 2-methylbicyclo[2.2.1]-2-heptanol, endo- (III) has been
studied by employing the deuterium labelling technique. The
results obtained indicate that the existence of nonclassical car-
bonium ion is of no significant importance during the fragment-
ation of the molecular ion of these alcohols and that the
dehydration of the molecular ion is stereospecific regarding the
position of eliminated hydrogen.

## INTRODUCTION

Bicyclo[2.2.1]-heptan derivates are compounds of considerable interest
from the chemical point of view and have been studied extensively in the
last ten years. A number of papers have also been published in connection
with their behaviour under electron impact in the ionization chamber of
a mass spectrometer for either analytical purposes or to establish relations
between their chemical and mass spectral behaviour[1-3]. A widely employed
and very useful method of obtaining the maximum information from mass
spectra is the application of the deuterium labelling technique. Deuterium
labelling (as well as labelling with other nuclei) has recently brought, besides
valuable information, a great deal of confusion into many well known
fragmentation mechanisms observed in the mass spectrometer. On the one
hand, extensive or even complete scrambling of hydrogens (and carbons)
observed in aromatic and heterocyclic molecular ions[4] makes the identification
of any particular fragments highly speculative, whereas on the other hand
some fragmentation which were earlier thought to be nonspecific to the
molecular structure are found to be stereospecific and/or selective. So the
general feeling that mass spectrometry has a small stereochemical potential
needs to be reconsidered. Recently, this subject was discussed by Green and
Roy[5] and evidence for hidden stereochemistry in mass spectrometry was
found in the case of the dehydration of isomers of substituted cyclohexanol.
Humski and Klasinc[6] studied the same process of dehydration in a number
of substituted bicyclo[2.2.1]-2-heptanols and found similar stereospecificity.

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Some other phenomena such as the classical-nonclassical controversy, retro-Diels-Alder reaction, Wagner-Meerwein rearrangement and the fragmentation pattern in this bicyclic system are still the subject of discussion. This paper deals with some of these problems, and a number of derivatives have been prepared in order to obtain more information on these processes in the mass spectrometer.

### RESULTS AND DISCUSSION

The mass spectra of bicyclo[2.2.1]-2-heptanol, *endo-* (I) and *exo-* (Ia), 1-methylbicyclo[2.2.1]-2-heptanol, *endo-* (II) and *exo-* (IIa), 2-methylbicyclo [2.2.1]-2-heptanol, *endo-* (III) as well as of I-3,3-$d_2$, I-2-d, Ia-3,3-$d_2$, II-7,7-$d_2$, IIa-7,7-$d_2$, II-*endo*-5,6-$d_2$ and III-*exo*-5,6-$d_2$ have been measured.
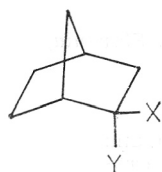


|  |  |  |  |
|---|---|---|---|
| X = H, | Y = OH; | bicyclo[2.2.1]-*endo*-2-heptanol | I |
| X = OH, | Y = H; | bicyclo[2.2.1]-*exo*-2-heptanol | Ia |

Mass spectra of I, I-2-*d* and I-3,3-$d_2$ are presented in Fig. 1. The spectra of I and Ia were identical as well as the spectra of I-3,3-$d_2$ and Ia-3,3-$d_2$. For these reasons the spectra of Ia and Ia-3,3-$d_2$ are not presented. Similarly, in Fig. 2 only the spectra of II, II-*endo*-5,6-$d_2$ and II-7,7-$d_2$ are reproduced since IIa and IIa-7,7-$d_2$ showed no difference from the corresponding endo compounds. Finally, in Fig. 3 the mass spectra of III and III-*exo*-5,6-$d_2$ are given. All these spectra are uncorrected and normalized to the base peak. The most characteristic masses are numbered.

*Mass Spectra of Compounds I, I-2-*d *and I-3,3-*$d_2$

These spectra are given in Fig. 1. From the occurrence of metastable ions in the first and second field-free region following scheme of the most important fragmentation pathways of this compound can be drawn (numbers represent $m/e$ ratios).

### SCHEME 1.

*Observed First Field-free Region Metastables*
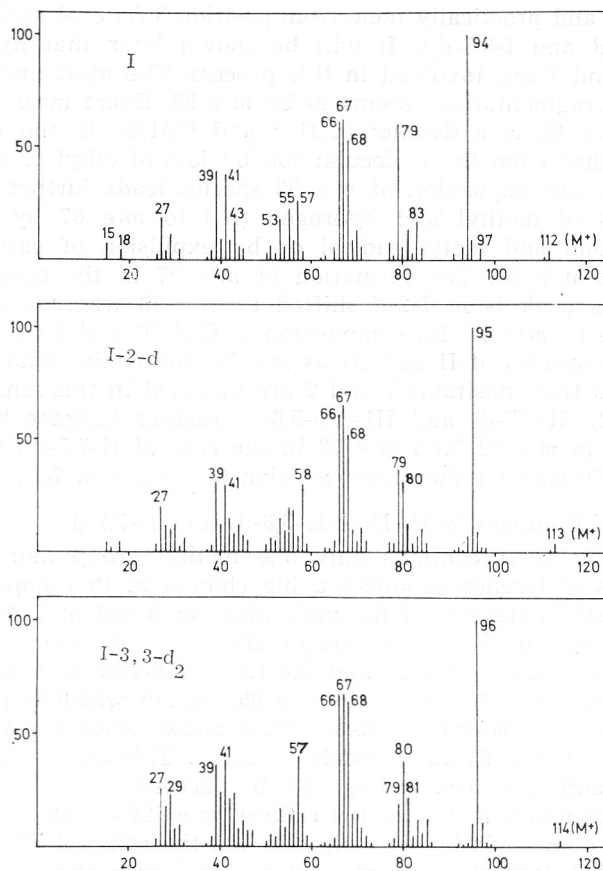Denoted by asterisk are second field-free metastables.
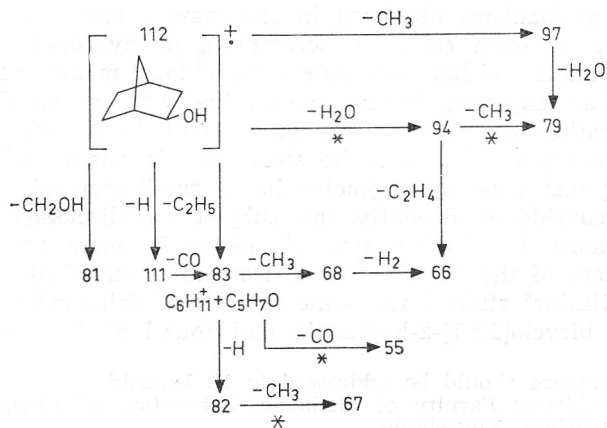
Fig. 1. The mass spectra of bicyclo[2.2.1]-*endo*-2-heptanol (I), I-2-*d* and I-3,3-d₂ at 70 eV.

The base peak in all three compounds is the [M-H$_2$O]-ion at $m/e$ 94, 95 and 96, respectively, thus showing no deuterium content in eliminated water. This ion decomposes further either by loss of a methyl group yielding $m/e$ 79, $m/e$ 79 and 80 and $m/e$ 79, 80 and 81, or by the loss of ethylene yielding $m/e$ 66, $m/e$ 66 and 67; and $m/e$ 66, 67 and 68 for I, I-2-*d* and I-3,3-$d_2$, respectively. Both processes show great involvement of hydrogens at positions 2 and 3. Thus, more than 50⁰/₀ of the methyl expelled from $m/e$ 95 of I-2-*d* contains deuterium from position 2, and about 75⁰/₀ of methyl expelled from $m/e$ 96 of I-3,3-$d_2$ contains deuterium from position 3 (in about 25⁰/₀ both deuteriums are involved). Besides water the molecular ion can expell hydrogen, methyl, ethyl and methoxyl radicals. All these competitive reactions were confirmed by metastable transitions (see Scheme 1). The hydrogen from position 2 is involved again in about 50⁰/₀ of methyl group loss (m. s. of I-2-*d*), while 50⁰/₀ of this group contains a hydrogen from position 3 (m. s. of I-3,3-$d_2$). As shown later (m. s. of II-7,7-$d_2$), this methyl group is probably formed from methylene at position 7 and one hydrogen either from position 2 or 3. On the other hand, most of the expelled ethyl groups contain very little hydrogen

from position 2 and practically none from position 3 (*m/e* 84 and *m/e* 85 in the spectra of I-2-*d* and I-3,3-*d₂*). It will be shown later that hydrogens from positions 5, 6 and 7 are involved in this process. The most important species in the further fragmentations seems to be *m/e* 83. Exact mass measurements showed that *m/e* 83 is a doublet ($C_6H_{11}^+$ and $C_5H_7O^+$ in the ratio of 5 : 1). It is formed either from the molecular ion by loss of ethyl or from [M-1] by decarbonylation. Decomposition of *m/e* 83 species leads further to *m/e* 66 by subsequent loss of methyl and hydrogen ($H_2$) to *m/e* 67 by two-step loss of hydrogen atom and metyl radical or by expulsion of carbon monoxide from $C_5H_7O^+$ to *m/e* 55. The formation of *m/e* 57 in the case of I is very interesting. This peak is in I-2-*d* shifted to *m/e* 58 whereas in the case of I-3,3-*d₂* remains at *m/e* 57. Its composition is $C_3H_5O^+$ and its counterpart can be found in the spectra of II and III as *m/e* 71, confirming that carbon atoms and substituents from positions 1 and 2 are included in this ion. Mass spectra of II-*endo*-5,6-*d₂*, II-7,7-*d₂* and III-*exo*-5,6-*d₂* further indicate by the partial shift of *m/e* 71 to *m/e* 72 (and *m/e* 73 in the case of II-7,7-*d₂*) that the third carbon in $C_3M_5O^+$ comes either from position 6 or position 7.

*Mass Spectra of Compounds II, II-endo-5,6-d₂ and II-7,7-d₂*

The molecule of II contains only one methyl group more, (position 1) than I, but this difference produces a big change in the shape of the mass spectrum. All fragmentations of the molecular ion found in I are still present in II, but the dehydration is no longer the most important fragmentation process. The base peak at *m/e* 81 and the first field-free metastable measurement indicate that it is formed from *m/e* 96, an ion which is practically not observed in the mass spectrum. Exact mass measurements have shown that the composition of *m/e* 81 corresponds to $C_6H_9^+$. This ion is the counterpart of *m/e* 67 in I and is formed analogously by successive loss of two hydrogen atoms, carbon monoxide and a methyl radical (*m/e* 126 → 125 → 97 → 96 → 81). Concerning the demethylation of molecular ion the comparison of II, II-*endo*-5,6-*d₂* and II-7,7-*d₂* indicates that at least one hydrogen of the methyl is from position 7. Thus, *m/e* 111 in II is shifted to *m/e* 113 in II-*endo*-5,6-dd₂ without the loss of deuterium, whereas no *m/e* 113 was observed in II-7,7-*d₂*.

Compounds II-*endo*-5,6-*d₂* and II-7,7-*d₂* showed a substantial loss of deuterium in the dehydration process. The loss of HOD from II-*endo*-5,6-*d₂* is especially important in comparison with the negligible HOD-loss from III-*exo*-5,6-*d₂*, indicating the stereospecificity of the dehydration process. On the other hand, the subsequent loss of methyl from the [M-water]-ions of II-*endo*-5,6-*d₂* and II-7,7-*d₂*, does not show any substantial involvement of the deuterium from the labelled positions. Neglecting the possibility of methyl group expulsion from position 1 and comparing these spectra with the spectra of I and its labelled analogues, it follows that this methyl group is formed from positions 2 and 3.

Ethyl loss from molecular ion of compounds I, I-2-*d* and I-3,3-*d₂* was already proved not to originate from positions 2 and 3. Labelling experiments in II bring further insight on the origin of the ethyl loss. Here *m/e* 97 in II is in the case of II-*endo*-5,6-*d₂* distributed over *m/e* 97 (50⁰/₀), 98 (25⁰/₀) and 99 (25⁰/₀), whereas in II-7,7-*d₂* over *m/e* 97 (50⁰/₀) and 98 (50⁰/₀). This is consistent with the assumption that the ethyl fragment is formed with the same probability from combinations of methylene groups at positions 5, 6 and 7, plus
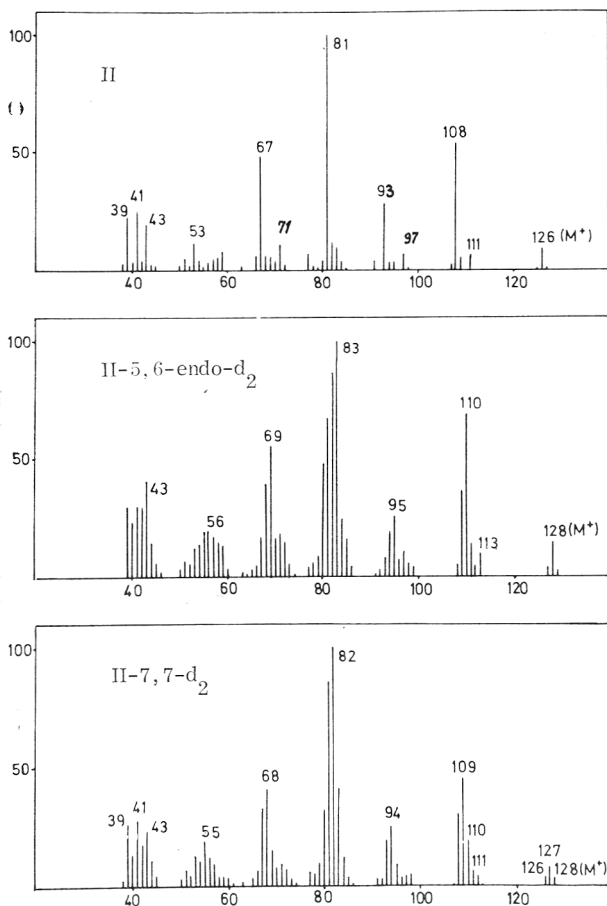
Fig. 2. The mass spectra of 1-methylbicyclo[2.2.1]-*endo*-2-heptanol (II), II-*endo*-5,6-$d_2$ i II-7,7-$d_2$
at 70 eV.

one hydrogen from the methylene group not involved (in the combination). Of minor importance but interesting is the formation of *m/e* 91 (tropylium ion?). First field-free metastable measurements indicate that it orignates from *m/e* 107 and 93, but unfortunately it was impossible to distinguish whether it loses oxygen or methane. Also the origin of *m/e* 107 was not established.

As in the case of I, the formation of *m/e* 67 from *m/e* 82 was found, and presumably originates from *m/e* 111 (*m/e* 111 → 83 → 82 → 67, see scheme 1).

*Mass Spectra of Compounds III and III-*exo*-5,6-$d_2$*

Compound III is a good example of the extreme influence which the introduction of a methyl group in a certain position can have on the mass spectrum. Although we can find here again most of the fragmentation processes discussed above for I and II, their mutual importance is dramatically changed. The loss of water, methyl, formyl (H + CO) and ethyl from the molecular ion are here processes of about the same probability. The formation
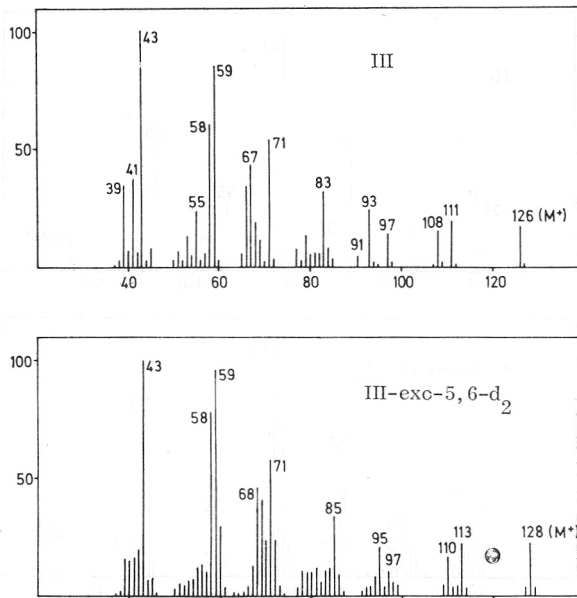
Fig. 3. The mass spectra of 2-methylbicyclo[2.2.1]-*endo*-2-heptanol (III) and III-*exo*-5,6-$d_2$ at 70 eV.

and further fate of the corresponding ions has been again investigated by first field-free metastable measurements. The results can be represented as follows (Scheme 2):
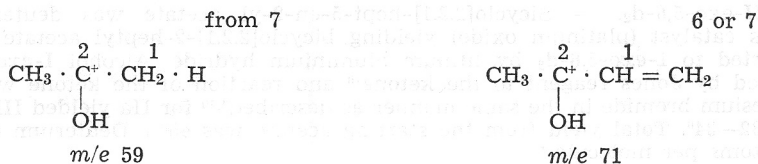
SCHEME 2.

*Observed First Field-free Region Metastables*
Denoted by asterisk are second field-free metastables.
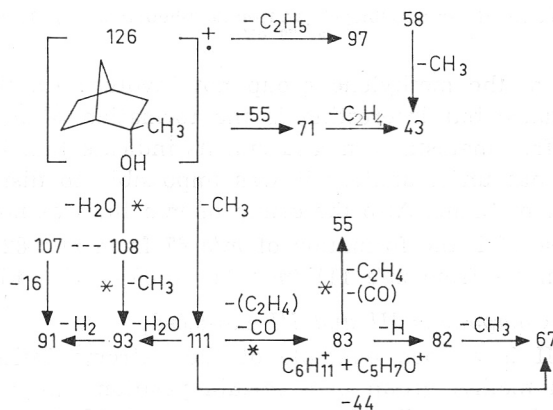


Unfortunately, these processes do not show the formation of all important ions e. g. *m/e* 59 observed in the spectrum of III. These ions probably generate from higher mass region than could be determined by metastable transitions

in our instrument $(m_2 \simeq 2m_1)$. The composition of the base peak at $m/e$ 43 corresponds to $CH_3CO^+$ containing probably carbon and its substituents in position 1. Analogously, and taking into account spectra of I ($m/e$ 57 and 45), II ($m/e$ 59 and 71) and their behaviour in deuterated derivatives, the following structures can be deduced for $m/e$ 59 and 71:

<div align="center">

from 7                                6 or 7

$$\overset{2}{CH_3} \cdot \overset{1}{\underset{\underset{OH}{|}}{C^+}} \cdot CH_2 \cdot H \qquad\qquad \overset{2}{CH_3} \cdot \overset{1}{\underset{\underset{OH}{|}}{C^+}} \cdot CH = CH_2$$

$m/e$ 59                                  $m/e$ 71

</div>

In the first field-free region only the formation of $m/e$ 71 was proved by metastable transition indicating its formation from molecular ion.

*Comparison of Mass Spectra of I, II and III*

A brief look at the spectra and at the structures of compounds I, II and III shows the great discrepancy between them: mass spectrometrically they behave as very different compounds, structurally they have the same bicyclic skeleton, II and III are even isomers. This difference indicates that the systems investigated are energetically and topologically extremely sensitive. A small change in energy and structure results in drastic change in fragmentation pathways. These pathways have shown to be strongly dependent on the position of substituents (loss of water, methyl, ethyl and other fragments). Contrary to expectations based on results in solution, none of these processes has shown the equivalence of positions 3 and 7 *i. e.* the existence of a non-classical carbonium ion structure. It is also surprising that there is no difference between the mass spectra of the *exo-* and *endo*-epimer of these alcohols. Maybe the study of some derivates could explain this behaviour. This work is in progress.

<div align="center">

EXPERIMENTAL

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All spectra were recorded under identical operating conditions with a CEC 21—110 C mass spectrometer at about $90^0$ with 70 eV, using a direct inlet rod or heated gas inlet system. The metastable peaks in the first field-free region were measured on the same instrument by decoupling of accelerating voltage[7]. Exact mass measurement were performed at a resolving power of approxim. 20.000.

*Bicyclo[2.2.1]-2-heptanol*, endo- *(I)* and exo- *(Ia)*, *I-3,3-d$_2$, Ia-3,3-d$_2$ and I-2-d.* — These compounds were prepared as described earlier[8]. I-3,3-$d_2$ and Ia-3,3-$d_2$ contained 1.99 atoms of deuterium per molecule.*

*2-Methylbicyclo[2.2.1]-2-heptanol*, endo- *(III).* — Compound III was prepared from bicyclo[2.2.1]-2-heptanon in $82^0/_0$ yield as described earlier[9], m. p. $32$—$33^0$.

*1-Methylbicyclo[2.2.1]-2-heptanol*, exo- *(IIa).* — Alcohol IIa was prepared in two steps in $75^0/_0$ yield by conversion of III to acetate ester by a previously described procedure[9] and subsequent saponification of the acetate with a solution of potassium hydroxide in methanol[10] yielding IIa, m. p. $72$—$73^0$.

*1-Methylbicyclo[2.2.1]-endo-2-heptanol (II).* — Alcohol IIa was oxidised to the ketone by Jones reagent[10] ($CrO_3$ in acetone). The ketone was reduced with lithium aluminium hydride yielding $65^0/_0$ of II, m. p. $85$—$86^0$.

*IIa-7,7-d$_2$.* — Bicyclo[2.2.1]-2-heptanon-3,3-$d_2$ was reduced with methylmagnesium bromide yielding, after the usual treatment[9], III-3-3-$d_2$, which was converted to

* according to mass spectral analysis

IIa-7,7-$d_2$, m. p. 71—73⁰ in the same way as described[9,10] for IIa. Deuterium content was rather poor with only 1.03 atoms per molecule.*

II-7,7-$d_2$. — Alcohol IIa-7,7-$d_2$ was converted[10] to the ketone by Jones regent. The ketone was reduced with lithium aluminium hydride in the usual manner yielding 63⁰/o of II-7,7-$d_2$, m. p. 84—86⁰. Deuterium content was 1.01 atom per molecule.*

III-exo-5,6-$d_2$. — Bicyclo[2.2.1]-hept-5-en-2-yl acetate was deuterated using Adams catalyst (platinum oxide) yielding bicyclo[2.2.1]-2-heptyl acetate which was converted to I-exo-5,6-$d_2$ by lithium aluminium hydride. Alcohol I-exo-5,6-$d_2$ was oxidized by Jones reagent to the ketone[10] and reaction of the ketone with methyl-magnesium bromide in the same manner as described[9,10] for IIa yielded III-exo-5,6-$d_2$, m. p. 32—34⁰. Total yield from the starting acetate was 45⁰/o. Deuterium content was 1.88 atoms per molecule.*

II-endo-5,6-$d_2$. — Compound III-exo-5,6-$d_2$ was converted to IIa-endo-5,6-$d_2$ in the same manner[9,10] as III to IIa. IIa-endo-5,6-$d_2$ was oxidized[10] with Jones reagent and obtained ketone was reduced by lithium aluminium hydride to II-endo-5,6-$d_2$, m. p. 85—87⁰. Deuterium content was 1.94 atoms per molecule.*

* according to mass spectral analysis

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## IZVOD

### Spektri masa biciklo [2.2.1]-2-heptanola

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Istraživani su spektri masa biciklo[2.2.1]-2-heptanola, *egzo-* i *endo-*, supstituiranih u položaju 1 ili 2 s metilnom skupinom. Obilježavanjem ovih alkohola s deuterijem u različitim položajima i analizom spektara masa ovih spojeva dobivene su fragmentacijske sheme. Dobiveni rezultati ukazuju da neklasični karbonium ion nema zamjetljivu ulogu u fragmentaciji molekularnih iona ovih spojeva i da je dehidratacija molekularnog iona stereospecifična s obzirom na položaj eliminiranog vodika.

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