

CCA-773

543.51:547.514.71

Original Scientific Paper

## Mass Spectra of Labeled Cyclopentanols\*

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Received November 27, 1972

The fragmentation of cyclopentanol has been studied by employing the deuterium labeling technique. Starting from the molecular ion the following specific processes could be established: loss of H from the position 1, loss of CH<sub>3</sub> formed mainly from 2 (or 5) position after  $\alpha$ -scission, loss of H<sub>2</sub>O as a 1,3-elimination, and loss of C<sub>2</sub>H<sub>5</sub> generated from 2 and 3 or 4 and 5 positions plus one hydrogen from position 5 or 2, respectively. The results are discussed.

### INTRODUCTION

Recently, it has been shown<sup>1,2</sup> that dehydration of the molecular ion of bicyclo[2.2.1]-2-heptanol in the mass spectrometer is a 1,3- and/or 1,4-elimination process. Regarding the loss of the second hydrogen, this reaction seems to be stereospecific. The first hydrogen exclusively comes from the hydroxyl group and the orientation of the hydroxyl group does not influence the mass spectrum. In the present study the mass spectral behaviour of cyclopentanol was investigated, employing deuterium labeling, field free metastable peak observation, and exact mass determination. Investigations of this kind have shown to give valuable information about fragmentation mechanisms<sup>3,4</sup> and the energetics thereof. The mass spectra of cyclopentanol and cyclopentanol-2,2,5,5-d<sub>4</sub>, and those of cyclic alcohols from C<sub>4</sub> to C<sub>8</sub>, have been already studied by Natalis<sup>5,6</sup>. A detailed study of the mass spectrum of cyclohexanol by means of deuterium labeling was performed by Budzikiewicz, *et al.*<sup>7</sup>

### RESULTS AND DISCUSSION

The mass spectra of cyclopentanol (I), cyclopentanol-*d* (I-*d*), cyclopentanol-1-*d* (I-1-*d*), cyclopentanol-2-*d*, *cis*- (I-*cis*-2-*d*) and *trans*- (I-*trans*-2-*d*), cyclopentanol-3,4-*d*<sub>2</sub> (mixture of *cis*- and *trans*-) (I-3,4-*d*<sub>2</sub>) and cyclopentanol-2,2,5,5-*d*<sub>4</sub> (I-2,2,5,5-*d*<sub>4</sub>) have been measured. The position of the deuterium label was proven by the NMR spectra of the mixture of cyclopentanol or deuterated cyclopentanols

\* Reported in part at the 3<sup>rd</sup> Yugoslavian Congress for Pure and Applied Chemistry, Ljubljana, June 1972.

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with the  $\text{Pr}(\text{DPM})_3^*$  complex. The ratio of deuterium in I-3,4- $d_2$  was 1.17/0.77 for the *trans/cis* positions towards the hydroxyl group. The spectra were assigned by inspection of the corresponding Dreiding models and the mathematic expression for the pseudocontact shifts<sup>8</sup>. The study of NMR spectra of the deuterated cyclopentanol gave the identical assignments. The uncorrected and normalized spectra of these compounds at ionizing potential of 70 eV are reproduced in Fig. 1. The most characteristic masses are numbered. The fragmentation pathway(s) are indicated by arrows and are confirmed by first field free region metastable peaks; second field free metastables are denoted by asterisk. The results indicate that four parallel processes are responsible for the fragmentation of the cyclopentanol molecular ion: a) the loss of a hydrogen atom, b) the loss of a methyl radical, c) the dehydration process and d) the loss of an ethyl radical. Process d) as first field free metastables show, is to a small extent also a two step loss of  $\text{C}_2\text{H}_4 + \text{H}$ .

As will be shown later, one of the most important characteristics of these processes is that they are well defined in respect to the origin of the expelled neutral fragment. For this reason also a number of exact mass determinations were performed and the mass spectra of I, (I-3,4- $d_2$ ) and (I-2,2,5,5- $d_4$ ) have also been investigated at ionizing potentials of about 10, 12, 15, and 20 eV.

#### a) *The Loss of Hydrogen*

As previously found on cyclohexanol<sup>7</sup>, the loss of hydrogen in cyclopentanol also occurs from position 1. Thus, in the case of I-1- $d$  the  $[\text{M}-1]$ -ion becomes an  $[\text{M}-2]$ -ion with about the same intensity, whereas in all other compounds the loss of hydrogen resembles that in the undeuterated compound.

#### b) *The Loss of Methyl*

A methyl radical loss from the molecular ion is indicated in the mass spectrum of I. Its relative importance within the range of ionizing energies between 10 eV and 70 eV remains the same as shown by the nearly constant relative intensity to the molecular ion of 1/3.

No further loss of a hydrogen is observed. Labeled compounds can give an answer about the origin of the expelled methyl, but care must be taken about possible interference of this process with the dehydration mechanism ( $\text{CD}_3$  has the same mass as  $\text{H}_2\text{O}$  or OD, and  $\text{CHD}_2$  the same as OH). Therefore also exact mass determination of the corresponding ions in the molecules containing two and four deuterium atoms have been performed. Thus,  $m/e$  71 in I-3,4- $d_2$  is a singlet peak corresponding to  $\text{C}_5\text{H}_7\text{D}_2$  *i. e.*  $[\text{M}-\text{OH}]$ , whereas in I-2,2,5,5- $d_4$  both  $m/e$  72 and  $m/e$  73 are doublets:  $m/e$  72 corresponds to  $\text{C}_4\text{H}_6\text{DO}$   $[\text{M}-\text{CD}_3]$  and  $\text{C}_5\text{H}_4\text{D}_4$   $[\text{M}-\text{H}_2\text{O}]$  in a ratio of 1/5, and  $m/e$  73 corresponds to  $\text{C}_4\text{H}_5\text{D}_2\text{O}$   $[\text{M}-\text{CHD}_2]$  and  $\text{C}_5\text{H}_5\text{D}_4$   $[\text{M}-\text{OH}]$  in a ratio of about 1/5. The observed relative loss of labeled methyl radicals  $\text{CH}_3 : \text{CH}_2\text{D}$  in I-1- $d$  (5 : 1), I-2- $d$  (1 : 1) and I-3,4- $d_2$  (2 : 1) is, within experimental error, consistent with the assumption that the  $\text{CH}_2$  group from position 2 (or 5) is the precursor of the expelled methyl, taking statistically one of the remaining hydrogens. Theoretically  $\text{CH}_3 : \text{CH}_2\text{D}$  ratios of 6 : 1 (I-1- $d$ ), 1 : 1 (I-2- $d$ ), and 5 : 2 (3,4- $d_2$ ) are expected. It might be expected that  $\alpha$ -cleavage precedes this process. Unfortunately the results on

\* Tris(dipivalomethanato)praseodymium(III).

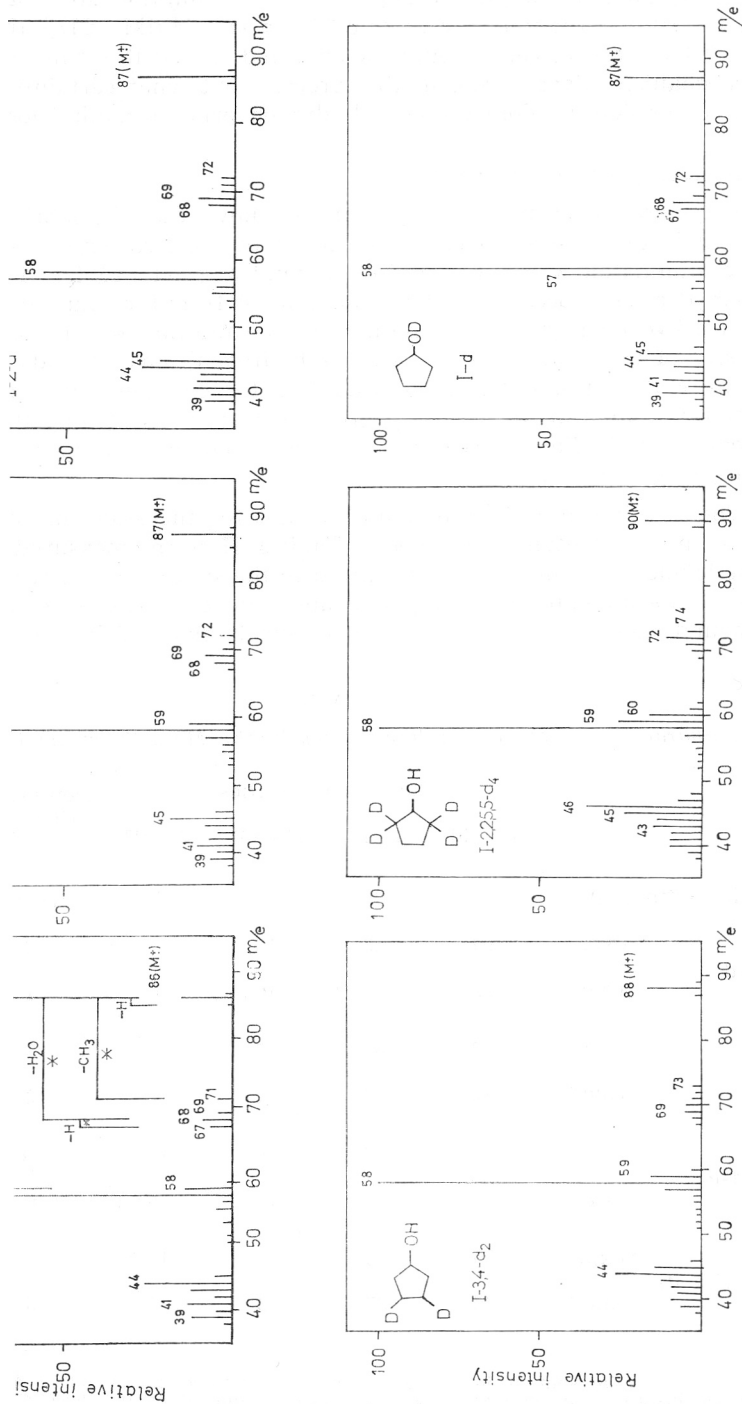


Fig. 1. The mass spectra of cyclopentanol (I), I-1-d, I-2-d, I-3,4-d<sub>2</sub>, I-2,2,5,5-d<sub>4</sub> and I-d at 70 eV.

I-2,2,5,5- $d_4$  do not completely support this assumption since about 1:2.5:0 intensity ratio of the ions  $m/e$  72,  $m/e$  73 and  $m/e$  74 ([M—CD<sub>3</sub>], [M—CD<sub>2</sub>H] and [M—CH<sub>2</sub>D]), respectively, would be expected. Thus, it seems that more than one mechanism plays a role in this process, but what certainly can be ruled out is a complete randomization of hydrogen prior to methyl loss.

### c) The Dehydration Process

The mass spectrum of cyclopentanol- $d$  shows that the label is removed by the dehydration process, *i. e.* the hydrogen of the hydroxyl group is included in the eliminated water. On the other hand a great problem in the study of the dehydration process in cyclopentanol arises from the unusually high further loss of a hydrogen (and even one more) from the [M—water]-ion. The relative intensity of [M—water] to [M—water—hydrogen]-ions depends highly on the ionizing energy ranging from 3:1 to 1:1 for energies between 10 to 70 eV respectively (*vide infra*). Here we give the results concerning the dehydration process at 70 eV. For the reasons mentioned some calculation was necessary to get an insight into this process.

The relative intensities of ions relevant for the study of the dehydration process in cyclopentanol are given in Table I. Here the measured ion intensities in the labeled compound are normalized to the sum of the corresponding intensities of the undeuterated compound and quoted as »experimental«. For each compound also the actual deuterium content is given. Taking into account this

TABLE I  
Dehydration of Labeled Cyclopentanols in the Mass Spectrometer at 70 eV

	Relative Intensities				Deuterium Content D, %	Loss of HOD	
	[M—18]	[M—19]	[M—20]	[M—21]			
Cyclopentanol (I)	100	76	9		100 D <sub>0</sub>	—	
I-1- $d$	exp. <sup>a</sup>	104	63	18	99 D <sub>1</sub>		
	calc. <sup>b</sup>	99	76	10	1 D <sub>0</sub>		
I-2- $d$	exp. <sup>a</sup>	103	65	17	97 D <sub>1</sub>	?	
	calc. <sup>b</sup>	97	77	11	3 D <sub>0</sub>		
I-3,4- $d_2$	exp. <sup>a</sup>	65	72	36	12	94 D <sub>2</sub>	yes
	calc. <sup>b</sup>	97	77	11		6 D <sub>1</sub>	
I-2,2,5,5,- $d_4$	exp. <sup>a</sup>	85	55	35	10	86 D <sub>4</sub>	?
	calc. <sup>b</sup>	86	87	13	1	13 D <sub>3</sub> 1 D <sub>2</sub>	

<sup>a</sup> Normalized to the sum of intensities of the undeuterated compound; <sup>b</sup> Assuming that the compound loses only undeuterated fragments as in I, and taking into account actual deuterium content.

content, the ion intensities for the relevant ions of the labeled compounds have been calculated assuming that only undeuterated fragments are lost in the same ratio as from the unlabeled compound. These values are quoted as »calculated« in Table I. An inspection of »experimental« *vs.* »calculated« values gives information about the loss of the label in the eliminated water. In this case [M—18] should be reduced on account of the [M—19] and lower mass ions. Now, Table I shows that this holds only for I-3,4- $d_2$ . Dehydration is again shown to take place as a 1,3-elimination process. But it is interesting to notice that I-1- $d$ , and I-2- $d$  showed loss of  $H_2O$  which was higher than calculated. This could be explained by competition of the fragmentation processes (isotope effect). The enhancement of the lower masses [M—20], [M—21] results from the subsequent loss of deuterium instead of hydrogen as calculated. Nevertheless, some possibility for a small fraction of 1,2-elimination could not be ruled out completely as it is indicated in Table I.

#### d) Loss of Ethyl Radical

The spectra of deuterated cyclopentanols in Fig. 1 and the intensities of the relevant ions in Table II show that the ethyl is formed from methylene groups 2 and 3 (or 4 and 5) and one hydrogen from position 5 (or 2, respectively), as suggested previously<sup>5-7</sup> and in accordance with the structure  $CH_2=CHCHOH$  for  $m/e$  57. Similarly, for  $m/e$  44 exact mass determinations yielded the composition  $C_2H_4O^+$  and from the mass spectra of the labeled compounds it can be found that positions 1 and 2 (5) generate this ion.

TABLE II

Loss of  $C_2H_5$  from Labeled Cyclopentanols in the Mass Spectrometer at 70 eV

	Relative Intensities				
	[M—28]	[M—29]	[M—30]	[M—31]	[M—32]
Cyclopentanol (I)	14	100			
I-1- $d$	13	100			
I-2- $d$	10	57	100		
I-3,4- $d_2$	2	15	100		
I-2,2,5,5- $d_4$		4	16	27	100

#### Low Energy Mass Spectra

Besides the expected reduction in the total ion current and enhancement in the relative intensity of the molecular ion (at about 8 eV it becomes the base peak), lowering of the ionizing voltage does not bring great changes in the fragmentations observed at 70 eV. A direct function of the ionizing energy are only the relative intensities of  $m/e$  39, 41, 43 and 67 in I, *i. e.* peaks which can be attributed to secondary fragmentations. Inspection of the dehydration process at lower energies which is now less disturbed by the loss of further hydrogen(s) shows clearly the loss of HOD only from the I-3,4- $d_2$  compound amounting to about 40% at 10 eV. Unfortunately, no information about possible higher

importance of the *cis* (or *trans*) position of deuterium relative to the hydroxyl group for dehydration could be obtained since our sample was a mixture of both.

## EXPERIMENTAL

*Technique*

The mass spectra were recorded under identical operating conditions with a CEC 21—110 C mass spectrometer at about 90 °C with 70 eV and a heated gas inlet system. The metastable peaks in the first field-free region were measured on the same instrument by decoupling the accelerating voltage. Exact mass measurements were performed at a resolving power of approximately 20,000.

The NMR spectra were recorded on a Jeol 100 MHz spectrometer. The concentrations of alcohol and Pr(DPM)<sub>3</sub>\* in CCl<sub>4</sub> were 0.2 M and 0.05 M respectively. Tetramethylsilane was used as an internal standard.

*Cyclopentanol (I)*. — Compound I, b. p. 139—40 °C, was prepared in 97% yield by lithium aluminum hydride reduction of cyclopentanone<sup>9</sup>. The NMR spectrum of the mixture of I and Pr(DPM)<sub>3</sub> complex was recorded and the following chemical shifts were obtained:  $\tau$  11.1, 2H, *trans*-3,4-H<sub>2</sub>;  $\tau$  12.3, 4H, *cis*-3,4-H<sub>2</sub> and *trans*-2,5-H<sub>2</sub>; and  $\tau$  15.1, 3H, 1-H and *cis*-2,5-H<sub>2</sub>.

*Cyclopentanol-1-d (I-1-d)*. — Alcohol I-1-d was obtained by lithium aluminum deuteride reduction of cyclopentanone in 93% yield<sup>9</sup>. The deuterium content was 0.99 atoms per molecule according to mass spectral analysis (Table I). The NMR spectrum of I-1-d and Pr(DPM)<sub>3</sub> showed the following chemical shifts:  $\tau$  11.1; 2H;  $\tau$  12.3, 1H;  $\tau$  15.1, 2H.

*trans-Cyclopentanol-2-d (I-2-d)*. — Alcohol I-2-d was prepared by the lithium aluminium deuteride reduction of cyclopentene oxide<sup>9</sup>, which was prepared in the usual manner by the oxidation of cyclopentene with perbenzoic acid.<sup>10</sup> The overall yield was 29%. The deuterium content was 0.97 atoms per molecule (Table I).

*3-Cyclopentanol*<sup>11</sup>. — This alcohol was prepared in 62% yield based on sodium borohydride (3.8 g, 0.1 moles) by the hydroboration of cyclopentadiene (45 g, 0.68 moles) and subsequent hydrolysis of the formed alkyl borane by a hydrogen peroxide-sodium hydroxide mixture. The product, b. p. 58—60 °C/20 mm, 5.44 g) was 76% pure according to GLC analysis (10% FFAP on 60/80 Chromosorb W). In order to obtain high purity, 2.3 g of the product was purified by preparative GLC (20% OS 138 on Chromosorb W 60/80 at 125 °C) giving 1.1 g of 3-cyclopentanol which was 99.0% pure (according to GLC analysis).

*Cyclopentanol-3,4-d<sub>2</sub> (I-3,4-d<sub>2</sub>)*. — 3-Cyclopentanol (0.4 g, 0.0048 moles) was refluxed for 2 hrs. with 7 ml of methanol-*d* (98.2% D) in order to exchange hydroxylic hydrogen with deuterium. Otherwise hydroxylic hydrogen could exchange with deuterium during the homogeneous catalytic deuteration and only partial deuteration could be achieved in position 3 and 4. Methanol was removed by distillation through a 30 cm Vigreux column. The residual 3-cyclopentanol-*d* was placed in a pear-shaped flask with 20 ml of methanol-*d* and 12 ml of dry benzene. Into this solution 0.092 g (10<sup>-6</sup> moles) of tris(triphenylphosphine)rhodium(I) chloride<sup>12,13</sup> was added and the flask was attached to the atmospheric pressure hydrogenation apparatus. The mixture was deuterated with 115 ml. (0.005 moles) of deuterium gas at room temp. by stirring for 18 hrs. The reaction mixture was distilled in high *vacuo* (10<sup>-5</sup> mm) at room temperature in order to separate the volatile components from the catalyst. The distillate obtained contained benzene, methanol-*d* and cyclopentane-3,4-d<sub>2</sub>-ol-*d*. The binary azeotropic mixture of methanol-benzene was distilled at 58 °C through a 30 cm Vigreux column. During the distillation 7 ml of methanol was added three times in order to exchange hydroxylic deuterium with hydrogen. When the temperature started to rise the mixture was free of benzene and the excess methanol was removed at 65 °C. The residue was purified by preparative GLC (20% OS 138) yielding 0.190 g of I-3,4-d<sub>2</sub>, 99.5% pure according to GLC analysis (10% FFAP). The deuterium content was 1.94 atoms per molecule (Table I). The NMR spectrum of I-3,4-d<sub>2</sub> with Pr(DPM)<sub>3</sub> gave the following signals:  $\tau$  11.1, 0.83 H;  $\tau$  12.3, 3.24 H;  $\tau$  15.1, 3H. That indicates that ~ 60% of deuteriums in position 3 and 4 is *trans* to the hydroxyl group (at  $\tau$  11.1) and ~ 40% *cis* (at  $\tau$  12.3).

\* Tris(dipivalomethanato)praseodymium(III).

*Cyclopentanol-2,2,5,5-d<sub>4</sub>* (I-2,2,5,5-d). — Compound I-2,2,5,5-d<sub>4</sub> was prepared in 21% yield by the base catalyzed hydrogen exchange of cyclopentanone with D<sub>2</sub>O and subsequent reduction of this ketone with lithium aluminium hydride<sup>9</sup>. The deuterium content was 3.85 atoms per molecule (Table I). The NMR spectrum of I-2,2,5,5-d<sub>4</sub> and Pr(DPM)<sub>3</sub> showed the following chemical shifts:  $\tau$  11.1, 2H;  $\tau$  12.3, 2H;  $\tau$  15.1, 1H.

*Cyclopentanol-d*. — The triple exchange of 0.778 g cyclopentanol with 7 ml D<sub>2</sub>O (98%) gave cyclopentanol-d with 67% deuterium in hydroxyl group according to NMR analysis.

## REFERENCES

1. K. Humski and L. Klasinc, *J. Org. Chem.* **36** (1971) 3057.
2. K. Humski, J. M. Jerkunica, L. Klasinc, and J. Marsel, *Croat. Chem. Acta* **44** (1972) 221.
3. J. L. Holmes and D. Mc Gillivray, *Org. Mass Spectrometry* **5** (1971) 1339 and 1349.
4. H. Güsten, L. Klasinc, J. Marsel, and D. Milivojević, *Org. Mass Spectrometry* **6** (1972) 175.
5. P. Natalis, *Bull. Soc. Chim. Belges* **69** (1960) 224.
6. P. Natalis, *Bull. Soc. Roy. Sci. Liège* **31** (1962) 790.
7. H. Budzikiewicz, Z. Pelah, and C. Djerassi, *Monatsh.* **95** (1964) 158.
8. J. K. M. Sanders and D. H. Williams, *J. Am. Chem. Soc.* **93** (1971) 641.
9. A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.* **80** (1958) 2326.
10. W. J. Hickinbottom, *Reactions of Organic Compounds*, Longmans Green and Co., London, New York, Toronto, 1950, p. 262.
11. H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.* **81** (1959) 247.
12. J. A. Osborn, *J. Am. Chem. Soc.* **93** (1971) 2397.
13. C. Djerassi and J. Gutzwiller, *J. Am. Chem. Soc.* **88** (1966) 4537.

## IZVOD

## Spektri masa obilježenih ciklopentanola

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Istraživani su spektri masa ciklopentanola obilježavanjem pojedinih mjesta s deuterijem. Na temelju dobivenih rezultata bilo je moguće dokazati nekoliko specifičnih procesa fragmentacije. To su gubitak vodika iz položaja 1, gubitak metila iz položaja 2 (ili 5), odlazak vode preko 1,3-eliminacijskog procesa i odlazak etila iz položaja 2 i 3 (ili 4 i 5) zajedno s jednim vodikom iz položaja 5 (ili 2).

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Primljeno 27. studenoga 1972.