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Chemical transformations of β-hydroxyethyl esters of n-2-hydroxyalkyl carbamic acids

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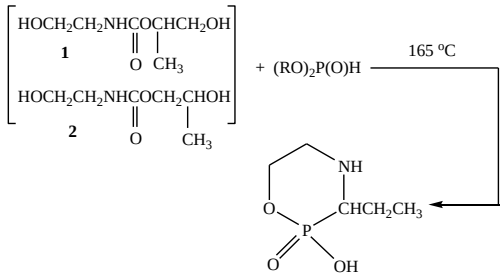
The reactivity of β–hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids at different temperatures was examined. It was established that β–hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids at 45ºC undergo several chemical transformations resulting in the formation of 2-oxazolidinones, 1,2-propandiol, 2-aminoethanol, N-2-hydroxyethyl carbamic acid and substituted 3-(2-hydroxyethyl) 2-oxazolidinones. At elevated temperatures (>150ºC) these esters afforded bis(2-hydroxyethyl) urea and N-(2-hydroxyethyl)-imidazolidinone. The reactivity enhancement of β–hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids may probably be explained through hydrogen bonding. The role of the hydroxyl group in these reactions may be regarded as intramolecular catalysis.

Key words: β–Hydroxyethyl esters of N-2-hydroxyalkyl derivatives of carbamic acid, chemical transformations.

INTRODUCTION

It has been recently reported that the reaction of H- phosphonic acid diesters {$(RO)_2P(O)H$, R = CH_3, C_2H_5, C_3H_7, *i*-C_3H_7, C_4H_9 and C_6H_5} with a mixture of 1-methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate and 2-methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate at elevated temperatures (>160ºC) resulted in 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane [1–3].



The formation of this cyclic aminophosphonic acid in 21% yield is unexpected having in mind the structure of the starting compounds. Obviously, the secondary reaction products resulting from the chemical transformations of the initial esters of carbamic acid react with the diesters of H-phosphonic acid to give 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane.

It is well known that amino alcohols of short chain length, when reacted with 1,3-dioxolan-2-on yielded β–hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids and the product distilled, gave cyclic urethanes [4,5]. For instance, 2-aminoethanol and 1,3-dioxolan-2-on at 45ºC yielded 2-oxazolidinone [4]; 4-amino-2-butanol and 3-amino-1-propanol gave six-membered cyclic urethanes. Facilitation of the alkaline hydrolysis of 1,2-diol monoesters is a well-established fact [6–9]. On the other hand it is known that the hydroxyl group in the esters of carboxylic acids plays an important role in amide-forming reactions [6–9].

In the present communication the chemical transformations of β–hydroxyethyl esters of N-2-hydroxyalkyl carbamic acid are studied.

EXPERIMENTAL

Materials:

Propylene carbonate (4-methyl-1,3-dioxolan-2-on) and ethylene carbonate (1,3-dioxolan-2-on) (Aldrich) were dried under vacuum. 2-Aminoethanol, 1-amino-2-propanol and 2-(methylamino)ethanol were purchased from Aldrich and were used as supplied.

NMR spectra were measured on a Bruker spectrometer at 250 MHz in $CDCl_3$ at 25ºC using TMS as an internal standard. FAB spectra were measured on a MAT 8200 spectrometer in glycerol.

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General procedure for the synthesis of β –hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids

β–Hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids were synthesized by reacting an equimolar amount of alkylene carbonate with aminoalcohol. Alkylene carbonate was added to aminoalcohol at temperatures below 10 ºC. After that the reaction mixture allowed to stay at 45ºC for 6 h.

*Synthesis of 1-methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate (**1**) and 2-methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate (**2**)*

A mixture of **(1)** and **(2)** was synthesized by reacting 4-methyl-1,3-dioxolan-2-on with 2-aminoalcohol.

1-Methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate **(1)**: ^{1}H NMR: δ = 1.20 (d, ^{3}J(H,H)=6.3 Hz, 3H, C*H*$_3$), 3.29 (q, ^{3}J(H,H)=5.04 Hz, 2H, CH$_2$C*H*$_2$NH), 3.64 (t, ^{3}J(H,H)=5.4 Hz, 2H, CH$_2$C*H*$_2$OH), 3.63–3.66 (dd, ^{3}J(H,H)=2.8 Hz, 2H, CHC*H*$_2$OH), 3.96–4.01 (m, 1H, C*H*), 4.24 (br s, O*H*), 6.19 ppm (t, ^{3}J(H,H)=5.4 Hz, N*H*); ^{13}C {H}NMR: δ = 16.83 (*C*H3), 43.67 (N*C*H$_2$), 61.63 (*C*H$_2$OH), 65.80 (CH*C*H$_2$OH), 72.72 (*C*H), 157.86 ppm (*C*=O).

2-Methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate **(2)**: ^{1}H NMR: δ = 1.17 (d, ^{3}J(H,H)=6.3 Hz, C*H*$_3$), 3.29 (q, ^{3}J(H,H)=5.04 Hz, 2H, CH$_2$C*H*$_2$NH), 3.64 (t, ^{3}J(H,H)=5.4 Hz, 2H, CH$_2$C*H*$_2$OH), 3.82–3.88 (m, 1H, C*H*), 4.04 , 4.07 (dd, ^{3}J(H,H)=2.8 Hz, 2H, OC*H*$_2$CH), 4.24 (brs, O*H*), 6.06 ppm (t, ^{3}J(H,H) = 5.4 Hz, 1H, N*H*). ^{13}C {H}NMR: δ =19.30 (*C*H$_3$), 43.61 (N*C*H$_2$), 61.63 (*C*H$_2$OH), 66.30 (*C*HOH), 70.30 (*C*H$_2$OC), 157.80 ppm (*C*=O); FAB-MS m/z=164.2.

*Synthesis of 2-hydroxyethyl-N-2'-hydroxyethyl carbamate (**3**)*

2-Hydroxyethyl-N-2'-hydroxyethyl carbamate **(3)** was synthesized from 1,3-dioxolan-2-on and 2-aminoethanol.

2-Hydroxyethyl-N-2'-hydroxyethyl carbamate **(3):** ^{1}H NMR: δ =3.29 (t, ^{3}J(H,H)=5.7 Hz, 2H, NHC*H*$_2$), 3.62 (t, ^{3}J(H,H)=5.8 Hz, 2H, C*H*$_2$OH), 3.74 (t, ^{3}J(H,H)=4.6 Hz, 2H, C*H*$_2$OH), 4.13 (t, ^{3}J(H,H)=5.6 Hz, 2H, (C(O)C*H*$_2$OH), 4.89 ppm (br s, 3H, O*H* and N*H*); ^{13}C {H} NMR: δ =37.29 (N*C*H$_2$), 59.64 (*C*H$_2$OH), 61.34 (CO*C*H$_2$), 157.99 ppm (*C*=O); FAB-MS m/z=150.1.

Synthesis of 1-methyl-2-hydroxyethyl-N-methyl-N-2'-hydroxyethyl carbamate (4) and 2-methyl-2-hydroxyethyl-N-methyl-N-2'-hydroxyethyl carbamate (5)

A mixture of **(4)** and **(5)** was synthesized by reacting 4-methyl-1,3-dioxolan-2-on with 2-(methylamino)ethanol.

1-Methyl-2-hydroxyethyl-N-methyl-N-2'-hydroxyethyl carbamate **(4):** ^{1}H NMR: δ =1.19 (d, ^{3}J(H,H)=6.3 Hz, 3H, C*H*$_3$), 3.18 (s, 3H, N-C*H*$_3$), 3.28 (t, ^{3}J(H,H)=5.1 Hz, 2H, C*H*$_2$N), 3.61 (t, ^{3}J(H,H)=5.4 Hz, 2H, C*H*$_2$OH), 3.66–3.68 (m, 2H, CHC*H*$_2$), 4.12– 4.15 (m, 1H, C*H*), 4.25 ppm (b.s. 2H, O*H*); ^{13}C {H} NMR: δ=16.79 (*C*H$_3$), 31.71 (N*C*H$_3$), 47.11 (NCH2), 59.78 (*C*H$_2$OH), 61.98 (CH*C*H$_2$OH), 70.81 (O*C*H), 157.22 ppm (*C*=O).

2-Methyl-2-hydroxyethyl-N-methyl-N-2'-hydroxyethyl carbamate **(5)**: ^{1}H NMR: δ =1.17 (d, ^{3}J(H,H)=6.3 Hz, 3H, C*H*$_3$), 3.18 (s, 3H, N-C*H*$_3$), 3.28 (t, ^{3}J(H,H)=5.1 Hz, 2H, C*H*$_2$N), 3.61 (t, ^{3}J(H,H)=5.4 Hz, 2H, C*H*$_2$OH), 3.81–3.91 (m, 1H, C*H*), 4.07–4.09 (m, 2H, OC*H*$_2$CH), 4.25 ppm (b.s. 2H, O*H*); ^{13}C {H} NMR: δ=19.07 (*C*H$_3$), 31.71 (N*C*H$_3$), 47.11 (N*C*H$_2$), 59.78 (*C*H$_2$OH), 61.98 (CH*C*H$_2$OH), 68.51 (O*C*H), 157.18 ppm (*C*=O); FAB-MS m/z = 178.1.

Synthesis of 2-hydroxyethyl-N-2'-hydroxypropyl carbamate (6)

2-Hydroxyethyl-N-2'-hydroxypropyl carbamate **(6)** was synthesized by reacting 1,3-dioxolan-2-on with 1-amino-2-propanol.

2-Hydroxyethyl-N-2'-hydroxypropyl carbamate **(6)**: ^{1}H NMR: δ =1.16 (d, ^{3}J(H,H)=6.3 Hz, 3H, C*H*$_3$), 2.97-3.03 and 3.18-3.27 (m, 2H, CHC*H*$_2$NH), 3.75 (t, ^{3}J(H,H)=4.4 Hz, 2H, C*H*$_2$OH), 3.83–3.93 (m, 1H, C*H*), 4.15 (t, ^{3}J(H,H)=5.0 Hz, 2H, COC*H*$_2$), 4.28 (b.s., 2H, O*H*), 6.18 ppm (t, ^{3}J(H,H)=5.7 Hz, 1H, N*H*); ^{13}C {H} NMR: δ=20.38 (*C*H$_3$), 48.21 (N*C*H$_2$), 60.81 (*C*H$_2$OH), 66.45 (C(O)*C*H$_2$), 66.83 (*C*HOH), 157, 64 ppm (*C*=O); FAB-MS m/z = 164.1.

Reactivity of β–hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids

1-Methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate (1) and 2-methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate (2) At 110 ºC

13.2 g (0.08 mol) of **1** and **2** were put into a three-necked flask equipped with a condenser, magnetic stirrer and thermometer. The reaction

mixture was heated at 110ºC for 1 h. After that the reaction mixture was allowed to cool to room temperature and was subjected to distillation.

Chemical transformations of *β*-hydroxyethyl esters of n-2-hydroxyalkyl carbamic acids *1,2-Propanediol* [2.4 g, 0.03 mol, 18,2 %, b.p. 34ºC (4.10^{-2} mm Hg)]; ^{1}H NMR: δ =1.13 (d, ^{3}J(H,H)=6.6 Hz, 3H), 3.22 – 3.49 (m, 2H), 3.70 –3.80 (m, 1H), 4.24 ppm (br s); ^{13}C NMR: δ =19.11 (CH_3), 68.19 (CH_2), 68.63 ppm (CH); *2-Oxazolidinone* [1.9 g, 0.022 mol, 14.4 %, b.p. 89ºC (4.10^{-2} mm Hg)]; ^{1}H NMR: δ =3.48–3.56 (m, 2H, NCH_2), 4.28–4.36 (m, 2H, OCH_2), 6.68 ppm (br s, 1H, N*H*); ^{13}C NMR: δ =42.01 (C4), 65.43 (C5), 161.15 ppm (C2); *2-Aminoethanol* [2.4 g, 0.04 mol, 18.2 %, b.p. 28 ºC (4.10^{-2} mm Hg)] were distilled. *Residue*, 6.5g.

At 155ºC

13.1 g, (0.08 mol) of **1** and **2** were heated at 155ºC for 2 h. During the heating CO_2 was evolved. After that the reaction mixture was allowed to cool to room temperature and was subjected to distillation.

1,2 –Propanediol [3.1 g, 0.04 mol, 23.7 %], *2-oxazolidinone* [3.4 g, 0.04 mol, 25.9 %] and a mixture of *5-methyl-3-(2-hydroxyethyl)-2-oxazolidinone* and *4-methyl-3-(2-hydroxyethyl)-2-oxazolidinone* [1.9 g, 0.01 mol, 16.4 %, b.p. 105 ºC (2.10^{-2} mm Hg)] were distilled; *5-Methyl-3-(2-hydroxyethyl)-2-oxazolidinone*, ^{13}C {H} NMR: δ =20.83 (*C*H_3), 44.02 (NCH_2), 46.88 (C4), 65.42 (*C*H_2OH), 70.96 (C5), 159.23 ppm (*C*=O). *4-Methyl-3-(2-hydroxyethyl)-2-oxazolidinone*, ^{13}C {H} NMR: δ =20.83 (CH_3), 52.48 (NCH_2), 44.02 (C4), 65.42 (*C*H_2OH), 59.86 (C5), 159.23 ppm (C=O). Residue, (3.5 g, 26.7 %).

1 and **2** were heated at 165ºC for 15 and 22 h. FAB-MS spectral data are given in Table 1.

2-Hydroxyethyl-N-2'-hydroxyethyl carbamate (3)

10.8 g (0.07 mol) of **3** were heated at 165ºC for 5 h. During the heating CO_2 was evolved. After that the reaction mixture was allowed to cool to room temperature and was subjected to distillation; *2-oxazolidinone* [1.5 g, 0.017 mol, 13.9%] and N-(2-hydroxyethyl)-2-oxazolidinone [0.8 g, 0.006 mol, 7.4 %, b.p. 112ºC (3.10^{-2} mm Hg)] were distilled. *N-(2-hydroxyethyl)-2-oxazolidinone* ^{13}C NMR: δ=44.02 (NCH_2), 46.88 (C4), 65.42 (*C*H_2OH), 70.96 (C5), 159.23 ppm (*C*=O). Residue, 8.2 g.

1-Methyl-2-hydroxyethyl-N-methyl-N-2'-hydroxyethyl carbamate (4) and 2-methyl-2-hydroxyethyl-N-methyl-N-2'-hydroxyethyl carbamate (5)

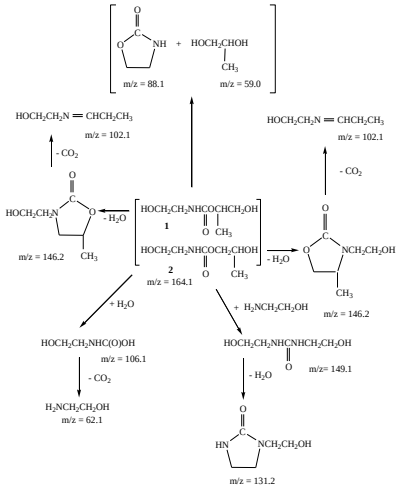
11.3 g (0.064 mol) of **4** and **5** were heated at 165ºC for 5 h. During the heating CO_2 was evolved. After that the reaction mixture was allowed to cool to room temperature and was subjected to distillation; *1,2-propanediol* (<0.5 g), *2-(methylamino)ethanol* [1.4 g, 0.018 mol, 12.4%] and *3-methyl-2- oxazolidinone* [3.5 g, 0.034 mol, 31.3%] were distilled. *3-Methyl-2-oxazolidinone* ^{1}H NMR: δ =3.48 -3.56 (m, 2H, NCH_2), 4.28–4.36 (m, 2H, OCH_2), 3.82 ppm (s, 3H, N-*C*H_3); ^{13}C{H} NMR: δ =47.80 (N-CH_3), 42.01 (C4), 65.43 (C5), 161.15 ppm (C2). Residue, 5.1 g.

2-Hydroxyethyl-N-2'-hydroxypropyl carbamate (6)

11.4 g (0.07 mol) of **6** was heated at 165ºC for 5 h. After that the reaction mixture was allowed to cool to room temperature and was subjected to distillation; *ethylene glycol* [1.6 g, 0.026 mol, 14.0%] and 5-methyl-2-oxazolidinone [2.5 g, 0.02 mol, 22.0%, b.p. 88 ºC (2.10^{-2} mm Hg)] were distilled. *5-Methyl-2-oxazolidinone*, ^{1}H NMR: δ=1.45 (d, ^{3}J(H,H)=3.8 Hz, 3H, CH_3), 3.65–3.71 (m, 2H, NCH_2), 4.73–4.81 (m, 1H, C*H*), 6.8 ppm (br. s, 1H, N*H*); ^{13}C {H} NMR: δ=20.84 (*C*H_3), 47.78 (N*C*H2), 73.90 (*C*H), 160.91 ppm (*C*=O). Residue, 7.3 g.

RESULTS AND DISCUSSION

Chemical transformations of 1-methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate and 2-methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate



Scheme 1. Chemical transformations of **1** and **2.**

Table 1. FAB-MS spectral data of the products obtained after heating of **1** and **2** at 45ºC, 110ºC, 155ºC and 165ºC. Peak intensities are given in parentheses.

Compound	$[M+H]^+$	45 °C	110 °C	155 °C	165 °C	
					15 h	22 h
1 and **2**	164.2	(100)	(100)	(65.7)	(20.7)	(3.3)
2-Oxazolidinone	88.1	(9.5)	(58.8)	(71.5)	(40.4)	(28.5)
1,2-Propanediol	59.1*	(3.2)	(17.5)	(12.1)	(9.8)	(6.4)
N-2-hydroxyethyl carbamic acid	106.1	(9.3)	(25.8)	(5.0)	(2.0)	(0.0)
2-Aminoethanol	62.1	(10.1)	(65.4)	(34.5)	(18.1)	(2.7)
Bis(2-hydroxyethyl) urea	149.1	(0.0)	(2.9)	(74.8)	(72.1)	(3.5)
N-2-hydroxyethyl imidazolidinone	131.2	(0.0)	(1.0)	(45.1)	(94.4)	(100)
5-Methyl-3-(2-hydroxy-ethyl)-2-oxazolidinone and 4-Methyl-3-(2-hydroxy-ethyl)-2-oxazolidinone	146.2	(6.8)	(10.5)	(84.4)	(100)	(27.4)
$HOCH_2CH_2N=CHCH_2CH_3$ (Shiff base)	102.1	(0.0)	(3.8)	(8.8)	(17.4)	(26.8)

* At the FAB conditions 1,2-propanol undergoes dehydration resulting in the formation of a cation with m/z = 59.1.

Study of the mixture of 1-methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate **1** and 2-methyl-2-hydroxyethyl-N-2'-hydroxyethyl carbamate **2** (m/z=164.2) after heating by FAB-MS revealed that depending on the temperature, several chemical reactions take place, resulting in the formation of new compounds (Scheme 1). The FAB-MS spectrum of the starting mixture of **1** and **2** showed that at 45ºC formation of a few compounds with m/z=88.1, 106.1, 146.2 proceeds. The mixture of **1** and **2** was heated at 165ºC for 15 and 22 h. FAB-MS spectral data are given in Table 1.

NMR studies of **1** and **2** after heating confirmed that several chemical reactions proceeded. ^{13}C {H}NMR spectrum (Fig. 1) revealed that several new carbonyl compounds are formed as a result of heating of **1** and **2**. The new signals at 159.02 ppm, 160.36 ppm, 161.1 ppm, and 164.04 ppm, characteristic for carbonyl carbon atoms appear after heating (Fig. 1b). The signals at 16.42 and 18.88 ppm for CH_3 carbon atoms of **1** and **2** (Fig. 1a) disappear (Fig. 1b). New signals at 18.68 ppm and 20.45 ppm which can be assigned to CH_3 carbon atoms appear (Fig. 1b). The intensity of the signal for NCH_2 carbon atoms of **1** and **2** (43.25 ppm and 43.31ppm) strongly decreases. New signals appear in the region 38.08 ppm – 46.48 ppm

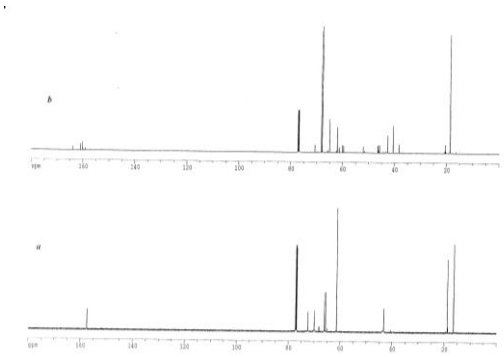
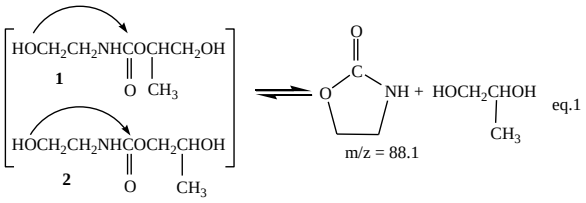
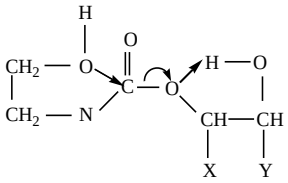


Fig. 1. ^{13}C {H}NMR spectrum of a mixture of **1** and **2**: (a) at 45 ºC and (b) after heating at 165ºC for 15 h.

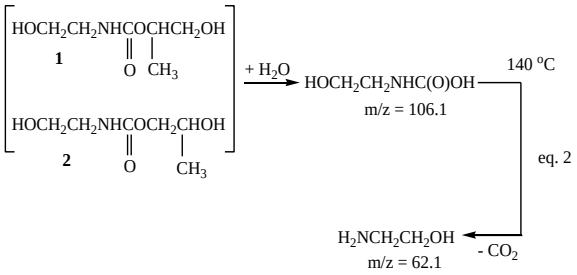
which are characteristics for NCH_2 carbon atoms. Signals at 69.98 ppm and 72.44 ppm for $C(O)OCH_2$ and $C(O)OCH$ carbon atoms disappear. In the ^1H NMR spectrum two doublets for CH_3 protons at 1.15 ppm and 1.18 ppm of **1** and **2** disappear. A new signal for CH_3 protons appears at 1.07 ppm. The characteristic signals at 5.82 and 5.98 ppm for C(O)NH protons of **1** and **2** disappear. A new signal at 5.95 ppm for NH protons appears. A few compounds were isolated by distillation. The intramolecular transesterification of **1** and **2** (by nucleophilic attack of 2'- hydroxyl group at the carbonyl group) yielded 2-oxazolidinone and 1,2-propanediol (eq.1).



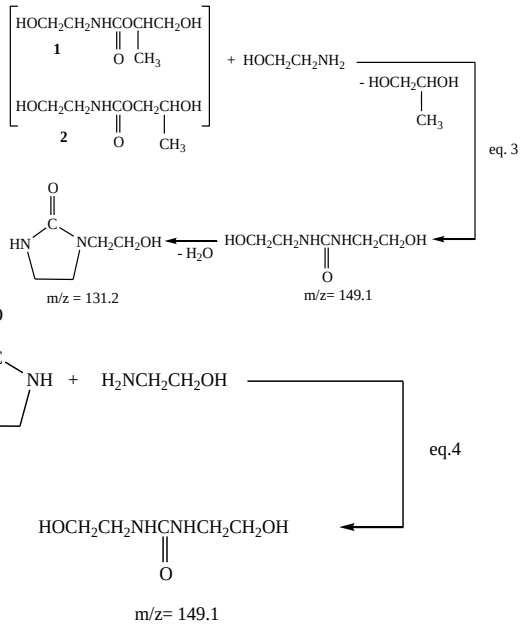
The signal at 161.1 ppm in the ^{13}C {H}NMR spectrum (Fig. 1b) can be assigned to the carbonyl atom of 2-oxazolidinone. The doublet at 1.13 ppm with $^{3}J(H,H)=6.6$ Hz can be assigned to the CH_3 group of 1,2-propanediol. 2-Oxazolidinone and 1,2-propanediol were isolated by vacuum distillation. The experimental results showed that the intramolecular transesterification proceeds at 45ºC. The reactivity enhancement of β -hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids is explicable in terms of hydrogen bonding of the β-hydroxyl group to the alcoholic oxygen. Such hydrogen bonding makes the carbonyl atom a stronger electrophilic center and favors the transesterification reaction at mild conditions.



The hydrolysis of **1** and **2** at 45ºC yielded N-2-hydroxyethyl carbamic acid (m/z 106.1). This acid decomposes at temperatures higher than 110ºC to 2-aminoethanol (m/z=62.1) and CO_2 (eq.2).



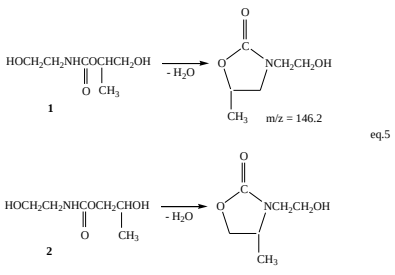
The peak with m/z=149.1 can be assigned to bis(2-hydroxyethyl)urea. This compound can be obtained *via* transesterification of **1** and **2** with ethanolamine (eq.3) or as a result of the reaction of 2-oxazolidinone with 2-aminoethanol (eq.4).



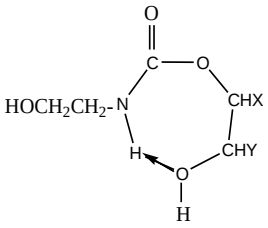
The experimental results revealed that the formation of bis(2-hydroxyethyl)urea *via* eq.4 is more acceptable at elevated temperatures.

The dehydration of bis(2-hydroxyethyl)urea, which starts at 110ºC, furnished N-(2-hydroxyethyl) imidazolidinone (m/z=131.2). At 165ºC after 22 h heating N-(2-hydroxyethyl) imidazolidinone was the main product (Table 1). It is known that higher temperatures [10] accelerate the dehydration of N-(2-hydroxyethyl)ureas to imidazolidinones. The experimental results showed that when heating at 165ºC is realized in the presence of a few drops of H_2SO_4 the main peak has m/z=131.2. We accept that H_2SO_4 catalyses the intramolecular transesterification of **1** and **2**, the transesterification of 2-oxazolidinone with 2-aminoethanol to form bis(2-hydroxyethyl)urea and its dehydration to N-(2-hydroxyethyl) imidazolidinone (m/z=131.2).

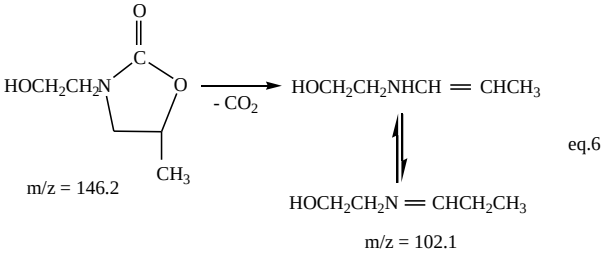
The FAB-MS spectrum showed a peak with m/z=146.2 which is the main peak at 165ºC and can be assigned to substituted 3-(2-hydroxyethyl)-2-oxazolidinones. 5-Methyl-3-(2-hydroxyethyl)-2-oxazolidinone and 4-methyl-3-(2-hydroxyethyl)-2-oxazolidinone result from the dehydration of **1** and **2** (eq.5).



The experimental results showed that the dehydration reaction starts at 45ºC and higher temperatures favour the dehydration of **1** and **2**. The participation of the NH proton in the hydrogen bonding with the oxygen atom of the *β* –hydroxyl group, favours the dehydration reaction, to yield substituted 3-(2-hydroxyethyl) -2-oxazolidinones.

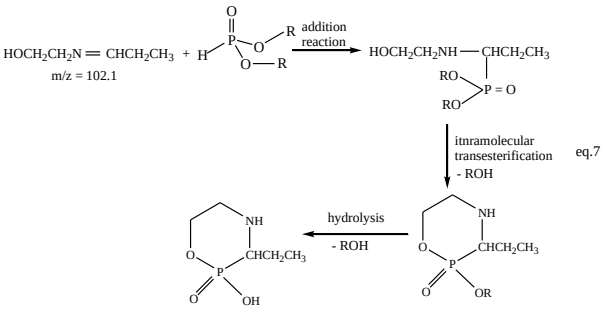


The substituted 3-(2-hydroxyethyl)-2-oxazolidinones are thermally unstable. The experimental results revealed that their content decreases (Table 1) from 100 % to 27.4 % at 165ºC after 22 h heating and their decomposition is accompanied by evolution of CO_2. The following reaction scheme for the decomposition of the substituted 3-(2-hydroxyethyl)-2-oxazolidinones can be accepted (eq. 6),



eq.6

In the FAB-MS spectrum a peak with m/z=102.1 appears which can be assigned to the Schiff base resulting from the decomposition of the substituted 3-(2-hydroxyethyl)-2-oxazolidinones. From the FAB-MS studies it can be seen that the content of this compound increases with the temperature increase. Unfortunately, we had no chance to isolate this compound. Indirect evidence for its formation is the isolated 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane (eq.7).



eq.7

Reactivity of 2-hydroxyethyl-N-2'-hydroxyethyl carbamate (3)

The experimental results show that 2-hydroxyethyl-N-2'-hydroxyethyl carbamate **3** undergoes the same reactions as **1** and **2**. The FAB-MS spectrum showed that during the synthesis of **3** (45ºC) there proceeds intramolecular transesterification yielding 2-oxazolidinone (m/z = 88). The FAB-MS spectral data showed that the main compound which forms at 165˚C is N-2-hydroxyethyl-imidazolidinone (m/z = 131.1).

Reactivity of 1-methyl-2-hydroxyethyl-N-methyl-N-2'-hydroxyethyl carbamate (4) and 2-methyl-2-hydroxyethyl-N-methyl-N-2'-hydroxyethyl carbamate (5)

The mixture of 1-methyl-2-hydroxyethyl-N-methyl-N-2'-hydroxyethyl carbamate and 2-methyl-2-hydroxyethyl-N-methyl-N-2'-hydroxyethyl carbamate was studied mainly because of the lack of NH proton in these carbamates. The experimental results showed that **4** and **5** undergo the same chemical transformation as **1**, **2** and **3**. The only difference with **1**, **2** and **3** is the absence of 3-substituted-2-oxazolidinones.

This result is a direct evidence for the participation of the NH proton of *β*–hydroxyethyl esters of N-2-hydroxalkyl derivatives of carbamic acid in a dehydration reaction yielding substituted 3-(2-hydroxyalkyl) 2-oxazolidinones.

Reactivity of 2-hydroxyethyl-N-2'-hydroxypropyl carbamate (6)

In 2-hydroxyethyl-N-2'-hydroxypropyl carbamate one of the hydroxyl groups is secondary. Therefore it was of interest to study the reactivity of this carbamate. 5-Methyl-2-oxazolidinone (m/z = 102) is the main compound which forms at 165ºC. The intramolecular transesterification of 2-hydroxyethyl-N-2'-hydroxypropyl carbamate starts at 45ºC.

CONCLUSION

The results obtained demonstrate that *β*–hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids are very reactive compounds at different temperatures. At mild conditions they undergo several chemical transformations. The specific reactivity of these esters of carbamic acids is determined by the presence of a *β* –hydroxyl group. The reactivity enhancement of *β*–hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids may be probably explained through

hydrogen bonding. The role of the hydroxyl group in these reactions may be regarded as intramolecular catalysis. The reaction temperature has an effect on the reactivity of the *β*–hydroxyethyl esters of N-2-hydroxyalkyl carbamic acids. Temperatures lower than 150ºC promote the intramolecular transesterification reaction resulting in the formation of oxazolidinones while temperatures higher than 150ºC favor the dehydration reaction leading to the formation of substituted 3-(2-hydroxyethyl) 2-oxazolidinones. Probably the decarboxylation of the substituted-3-(2-hydroxyethyl)-2-oxazolidinone at elevated temperatures furnished a Schiff base which reacted with H-phosphonic acid diesters to give 1,4,2-oxazaphosphorinane.

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ХИМИЧНИ ТРАНСФОРМАЦИИ НА *β*-ХИДРОКСИЕТИЛОВИ ЕСТЕРИ НА N-2-ХИДРОКСИАЛКИЛ КАРБАМИНОВИ КИСЕЛИНИ

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(Резюме)

Изследвана е реактивоспособността на *β*-хидроксиетилови естери на N-2-хидроксиалкил карбаминови киселини при различни температури. Установено е че *β*-хидроксилестерите of N-2-хидроксиакил карбаминови киселини при 45ºC претърпяват няколко химични трансформации, даващи 2-оксазолидони, 1,2-пропандиол, 2-сминоетанол, N-2-хидроксиетил карбаминова киселина и заместени 3-(2-хидроксиетил) 2-оксазолидони. При по-високи температури (>150ºC) тези естери these esters afforded бис(2-хидроксиетил) карбамид и N-(2-хидроксиетил)-имидазолидон. Повишаването на реактивоспособността на *β*-хидроксиетиловите естери на N-2-хидроксиалкил карбаминовите киселини вероятно може да се обясни чрез образуване на водородни връзки. Ролята на хидроксилните групи при тези реакции може да се отнесат към интрамолекулния катализ.

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