

Synthesis and Some Reactions of Polyols Formals

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Abstract—Synthesis of formals of some polyols such as dipentaerythritol, dietriol and diglycerin was proposed. Based on them, esters and carbamates were obtained.

Keywords: dipentaerythritol, di(trimethylol propane), diglycerol, isocyanate, monochloroacetic acid chloride

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It is known that condensation of triols with carbonyl compounds gives rise to the mixtures of 5- and 6-membered 1,3-dioxacycloalkanes [1, 2]. These compounds and their derivatives are used as components of motor fuels, corrosion inhibitors, as well as reagents in the synthesis of pharmaceutical drugs [3, 4]. Cyclic acetals of 1,1,1-trioxymethylalkanes and dipentaerythritol have found application as components of polymer materials and coatings [5, 6]. In recent years, production volume and fields of application of ethers and esters, amines and other mono-, oligo- and polymer compounds on the basis of tetra- and hexaols—dimers of glycerol, di(trimethylol propane), and pentaerythritol are expanded [7, 8]. In this connection, we have studied condensation of polyols – dipentaerythritol **1**, di(trimethylol propane) **2** and diglycerol **3** with paraform **4** and performed some transformations of the obtained heterocyclic alcohols (formals of dipentaerythritol **5**).

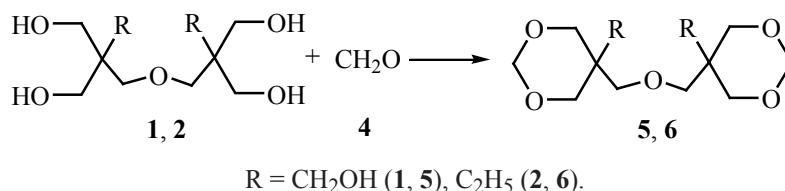
Condensation of polyols **1**, **2** with paraform **4** in the presence of 1% sulfuric acid at 80°C affords formals of dipentaerythritol **5** and di(trimethylol propane) **6** in 75 and 90% yield, respectively (Scheme 1). Using the method of concurrent reactions, by comparing the yields of formals **5** and **6** in the reaction of condensation of polyols **1** and **2**

with paraform **4**, di(trimethylol propane) **2** was shown to be 4 times more active than dipentaerythritol **1** (ratio of the reagents **1** : **2** : **4** = 1 : 1 : 0.5). According to the data of chromatomass spectrometry and NMR spectroscopy, heterocycles **5** and **6** are formed as mixtures of isomers **5a**, **5b** and **6a**, **6b** in the ratio of 3 : 1 and 6 : 5 respectively (Scheme 2).

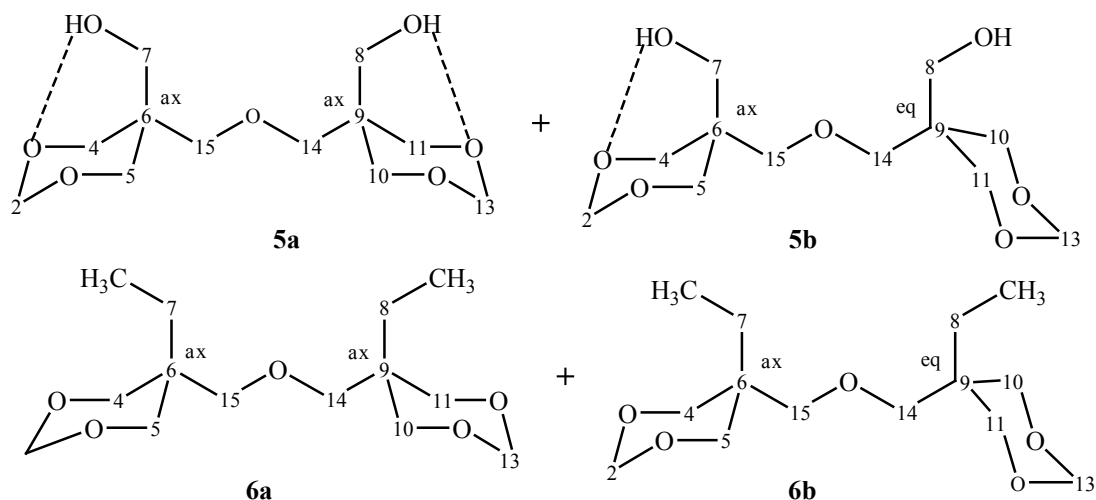
Isomers **5a**, **5b** and **6a**, **6b** differ in orientation of substituent R (CH₂OH for **5a**, **5b** and C₂H₅ for **6a**, **6b**) in position 5 of the ring – diaxial orientation in **5a** and **6a** or axial-equatorial in **5b** and **6b**. Three-fold prevalence of isomer **5a** over **5b** is explained by the presence of two intramolecular hydrogen bonds for the diaxial orientation of CH₂OH group. There is no intramolecular interaction in the di(trimethylol propane) derivative **6**, so, the content of stereoisomers **6a** and **6b** with diaxial and axial-equatorial orientation of the C₂H₅ groups is practically equal.

The structure of the obtained heterocycles **5a**, **5b** and **6a**, **6b** was proved by the method of ¹H and ¹³C NMR spectroscopy. The signals in the molecules of formals were assigned based on the analysis of chemical shifts and SSCC between the protons of the heterocyclic fragment (Table 1). In the ¹H NMR spectrum of formals of dipentaerythritol **5a**, **5b** the signals of methylene protons

Scheme 1.



Scheme 2.



of C⁷H₂OH and C⁸H₂OH groups appear, respectively, at 3.66 ppm and 3.68–3.70 ppm, thus suggesting the presence of two stereoisomers. The protons of the ether group CH₂O in **5a** resonate at 3.52 ppm, and in **5b**, at 3.54 ppm. From the integral intensity of the OH group protons, the ratio of stereoisomers **5a** : **5b** = 3 : 1. The

predominance of the diaxial stereoisomer **5a** is explained by its stabilization due to the intramolecular hydrogen bond.

In the ¹³C NMR spectra the values of chemical shifts of the chiral carbon atoms C⁶ and C⁹ are equal to 39.8 (**5a**) and 39.0 (**5b**) ppm. Carbons C^{7,8} at the OH group in

Table 1. NMR data for formals of dipentaerythritol **5a**, **5b** and di(trimethylol propane) **6a**, **6b**

Atom no.	5a		5b		6a		6b	
	δ_{H} , ppm (<i>J</i> , Hz)	δ_{C} , ppm	δ_{H} , ppm (<i>J</i> , Hz)	δ_{C} , ppm	δ_{H} , ppm (<i>J</i> , Hz)	δ_{C} , ppm	δ_{H} , ppm (<i>J</i> , Hz)	δ_{C} , ppm
2	4.57 s	94.1	4.57 s	94.0	4.65 d, 4.85 d (<i>J</i> = 6.0)	94.1	4.60 d, 4.80 d (<i>J</i> = 4.0)	94.1
4	3.41–3.44 m	69.6	3.41–3.44 m	69.4	3.40–3.50 m	72.2	3.40–3.50 m	72.2
5								
6	–	39.8	–	39.7	–	37.4	–	37.5
7	3.66 s	62.2	3.70 s	63.4	1.30 q (<i>J</i> = 4.0)	24.2	1.25 q (<i>J</i> = 7)	23.0
8								
9	–	39.8	–	39.7	–	37.4	–	37.5
10	3.41–3.44 m	69.6	3.41–3.44 m	69.4	3.40–3.50 m	72.2	3.40–3.50 m	72.2
11								
13	4.75 s	94.1	4.79 s	94.0	4.65 d, 4.85 d (<i>J</i> = 6)	94.1	4.60 d, 4.80 d (<i>J</i> = 4)	94.1
14	3.52 s	70.9	3.54 s	69.4	3.80 s	66.1	3.77 s	66.1
15								
16	–		–		0.85 t (<i>J</i> = 7)	7.1	0.85 t (<i>J</i> = 7)	7.5
17	–		–					
OH	2.93 s	–	2.89 s 2.87 s	–	–		–	

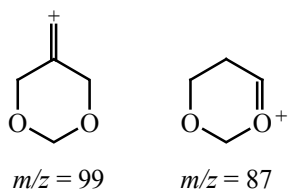
Table 2. NMR data for compounds **8a**, **8b** and **10a**, **10b**

Atom no.	8a		8b		10a		10b	
	δ_{H} , ppm (J , Hz)		δ_{H} , ppm (J , Hz)	δ_{C} , ppm	δ_{H} , ppm (J , Hz)	δ_{C} , ppm	δ_{H} , ppm (J , Hz)	δ_{C} , ppm
2	4.80 d ($J = 5.0$)	94.2	4.55 d ($J = 3.3$)	94.2	4.95 s	93.9	4.95 s	93.9
4	3.40–3.43 m	69.1	3.40–3.43 m	69.2	3.60–3.65 m	69.1	3.60–3.65 m	68.8
5								
6	–	41.0	–	40.9	–	39.1	–	39.1
7	3.75 s	64.7	3.75 s	63.8	4.00 s	63.4	4.00 s	63.1
8								
9	–	41.0	–	40.9	–	39.1	–	39.1
10	3.40–3.43 m	69.1	3.40–3.43 m	69.2	3.60–3.65 m	69.1	3.60–3.65 m	68.8
11								
13	4.80 d ($J = 5.0$)	94.2	4.55 d ($J = 3.3$)	94.2	4.95 s	93.9	4.95 s	93.9
14	4.25 s	70.0	4.25 s	70.0	4.38–4.42 m	70.5	4.38–4.42 m	70.5
15								
16, 17	–	166.8	–	167.0	–	153.8	–	153.7
18, 19	4.10 s	38.8	4.10 s	38.8	8.10 s	–	8.10 s	–
20–31	–		–		7.46–7.80 m	118.4–140.5	7.46–7.80 m	118.4–140.5

stereoisomer **5a** resonate at 62.2 ppm, and in the axial-equatorial stereoisomer **5b**, at 63.4 ppm.

In the ^1H NMR spectrum of the mixture of formals of di(trimethylol propane) **6a**, **6b** the signals of the C^7H_2 and C^8H_2 groups are observed at 1.25 (for the minor axial-equatorial stereoisomer **6b**) and 1.30 ppm (for the predominant diaxial stereoisomer **6a**). The signals of the protons of the CH_2O ether groups for the diaxial stereoisomer **6a** and axial-equatorial stereoisomer **6b** were registered at 3.77–3.80 ppm. In the ^{13}C NMR spectra of compounds **6a**, **6b**, the signals of the C^6 and C^9 atoms are observed at 37.4–37.5 ppm. Atoms $\text{C}^7,8$ in stereoisomer **6a** resonate at 24.2 ppm, in the axial-equatorial stereoisomer **6b**, at 23.0 ppm.

Ionization of formals **5a**, **5b** and **6a**, **6b** proceeds via the formation of ion with $m/z = 99$ (Scheme 3). Its

Scheme 3.

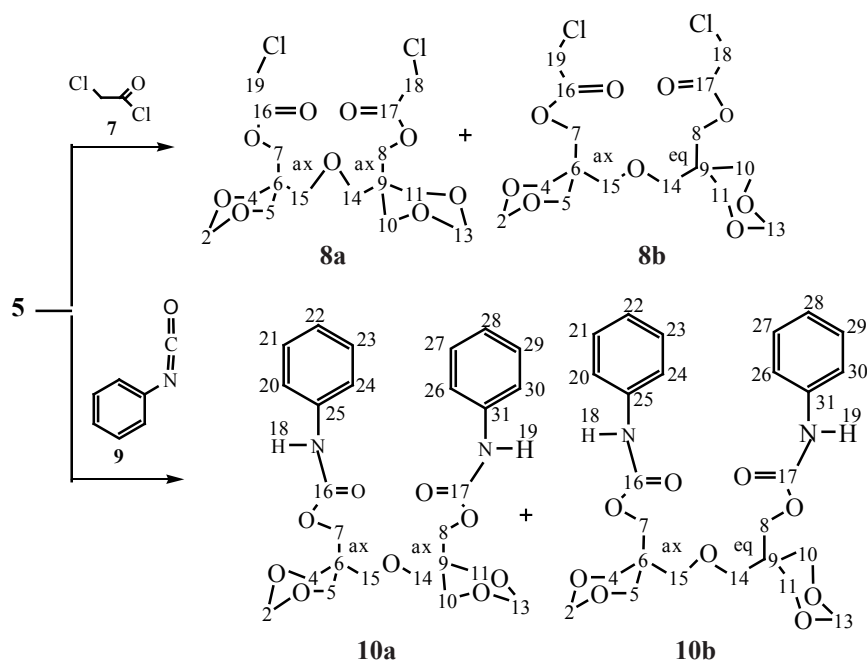
intensity is 100% (**5a**), 60% (**5b**), 94% (**6a**) and 96% (**6b**). The molecular ion is most stable in molecules **6a** (274/2) and **6b** (274/1), whereas for the derivatives of dipentaerythrol **5a**, **5b** the molecular ion was not detected. Characteristic ion $m/z = 87$ is registered only in molecules **5a** (10%) and **5b** (100%).

By acylation of the hydroxyl groups of diol **5** with chloroacetic chloride **7** in pyridine at 50°C ester **8** was obtained in quantitative yield as a mixture of isomers **8a** and **8b** in the ratio **8a** : **8b** = 3 : 1. With isocyanate **9** (hexane, 30°C), compound **5** forms urethane **10** in 80% yield (**10a** : **10b** = 3 : 1). The ratio of the isomers of esters **8a**, **8b** and urethanes **10a**, **10b** coincides with that in the starting diol **5**. Apparently, the activity of the axial and equatorial CH_2OH groups in the studied reactions is similar (Scheme 4). ^1H and ^{13}C spectral characteristics of esters **8a**, **8b** are given in Table 2.

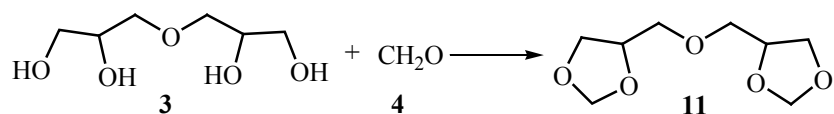
Condensation of diglycerol **3** with paraform **4** in benzene at 70°C quantitatively led to bicyclic 1,3-dioxolane **11** (Scheme 5).

From the data of chromatomass spectrometry and NMR spectroscopy, compound **11** exists in the form of

Scheme 4.



Scheme 5.



two diastereomers in the ratio **11a** (*erythro*) : **11b** (*treo*) = 5 : 4 (Scheme 6).

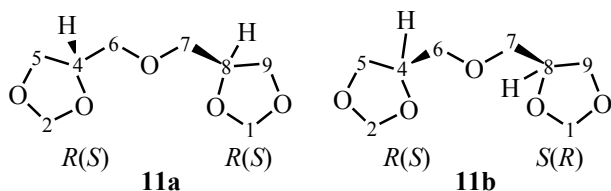
The presence of multiplets of the C⁴H and C⁸H groups in isomers **11a** (3.40–3.42 ppm) and **11b** (4.10–4.13 ppm) in the ¹H NMR spectra of formal of diglycerol are indicative of the presence of stereoisomers with configuration of the chiral centers in molecule **11a** (*RS,RS*), *erythro*-isomer and in molecule **11b** (*RS,SR*), *treo*-isomer. Protons of the C²H₂ group of 1,3-dioxolane

fragment in isomer **11a** appear as two doublets at 4.61 ppm and at 4.78 ppm with SSCC 2.7 Hz. Protons of the C⁵H₂ group of 1,3-dioxolane fragment in isomer **11a** are registered as a multiplet at 3.47–3.54 ppm. Protons of the C²H₂ group of 1,3-dioxolane fragment in isomer **11b** are observed as two doublets at 4.78 and 4.91 ppm with SSCC 3.1 Hz. Protons of the C⁵H₂ group of 1,3-dioxolane fragment in isomer **11b** appear as a multiplet at 3.47–3.54 ppm, similar to the signals of isomer **11a** (Table 3).

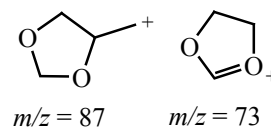
Table 3. NMR data for the isomers of diglycerol **11a**, **11b**

Atom no.	11a		11b	
	δ_{H} , ppm (<i>J</i> , Hz)	δ_{C} , ppm	δ_{H} , ppm (<i>J</i> , Hz)	δ_{C} , ppm
2	4.61 d, 4.78 d (<i>J</i> = 2.7)	93.3	4.78 d, 4.91 d (<i>J</i> = 3.1)	95.1
4	3.40–3.42 m	70.3	4.10–4.13 m	74.2
5	3.47–3.54 m	69.4	3.47–3.54 m	71.6
6	3.56–3.98 m	66.2	3.56–3.98 m	69.9
7	3.40–3.42 m	70.3	4.10–4.13 m	74.2
8	3.47–3.54 m	69.4	3.47–3.54 m	71.6
11	4.61 d, 4.78 d (<i>J</i> = 2.7)	93.3	4.78 d, 4.91 d (<i>J</i> = 2.3)	95.1

Scheme 6.



Scheme 7.



From the integral intensity of the protons of the C⁴H group, the ratio of the isomers **11a** : **11b** is 6 : 5.

In the ¹³C NMR spectra of formals of diglycerol **11a**, **11b** the signals of atoms C⁴ and C⁸ appear at 70.3 (**11a**) and 74.2 ppm (**11b**). The signals of carbon atoms C² and C¹¹ of the 1,3-dioxolane ring are observed at 93.3 (**11a**) and 95.1 ppm (**11b**). The signals of the ether group C⁶ and C⁷ are registered at 66.2 ppm (**11a**) and 69.9 ppm (**11b**).

Ionization of diglycerol formals **11a,b** proceeds with the formation of the same fragment ions differing only in the intensity (Scheme 7). For the *erythro*-isomer **11a**, maximum intensity is observed for ions with $m/z = 87$ and 73, whereas for the *threo*-isomer **11b** maximum intensity (100%) has only the ion with $m/z = 87$. The molecular ion with $m/z = 190$ is more stable in isomer **11a** (5%), whereas its intensity in the *threo*-isomer **11b** is 1%.

Therefore, we have synthesized formals of dipentaerythritol, diglycerol, and di(trimethylol propane), whose structure was analyzed by the methods of NMR spectroscopy and chromatomass spectrometry. On the basis of formal of dipentaerythritol, the esters and carbamates were synthesized.

EXPERIMENTAL

Chromatography analysis of the reaction products was carried out on a HRGC 5300 Mega Series Carlo Erba chromatograph with flame-ionization detector (gas-carrier—helium, 30 mL/min, column of 25 m length, temperature programming mode with heating from 50 to 280°C with the rate 8 deg/min). Mass spectra were obtained on a Crystal-5000 M instrument (gas-carrier—helium, capillary column of 30 m length, column temperature from 80 to 280°C with the rate 20°C/min, temperature of the transition line 300°C, temperature of the ion source 300°C). NMR spectra were registered on a Bruker AVANCE-500 spectrometer (¹H 500.13 MHz) in CDCl₃.

General procedure for the synthesis of formals of dipentaerythritol (5a, 5b), di(trimethylol propane) (6a, 6b), and diglycerol (11a, 11b). The mixture of 0.02 mol of alcohol, 0.06 mol of paraform, 0.2 g of sulfuric acid,

40 mL of benzene (in the case of dipentaerythritol the mixture of DMF and benzene) was stirred at 80°C for 3–8 h until the calculated amount of water was evolved. After completion of the reaction, the mixture was dried with CaCl₂, filtered and evaporated on a rotary evaporator. The reaction products were isolated by vacuum distillation.

Oxybis(methylene-1,3-dioxane-5,5-diyl)dimethanol (5a). Mass spectrum, m/z (I_{rel} , %): 159 (10), 147 (60), 129 (25), 99 (100), 87 (10), 69 (60), 57 (20), 41 (60).

Oxybis(methylene-1,3-dioxane-5,5-diyl)dimethanol (5b). Mass spectrum, m/z (I_{rel} , %): 159 (12), 147 (30), 129 (20), 99 (60), 87 (100), 69 (75), 57 (10), 41 (30).

5,5-[Oxydi(methylene)]bis(5-ethyl-1,3-dioxane) (6a). Mass spectrum, m/z (I_{rel} , %): 274 (2) [M^+], 147 (90), 129 (50), 99 (96), 69 (96), 57 (75), 41 (100).

5,5-[Oxydi(methylene)]bis(5-ethyl-1,3-dioxane) (6b). Mass spectrum, m/z (I_{rel} , %): 274 (1) [M^+], 147 (45), 129 (25), 99 (94), 69 (80), 57 (80), 41 (100).

4,4-[Oxydi(methylene)]bis-1,3-dioxolane (11a). Mass spectrum, m/z (I_{rel} , %): 190 (5) [M^+], 189 (3), 117 (12), 101 (3), 87 (100), 73 (100).

4,4-[Oxydi(methylene)]bis-1,3-dioxolane (11b). Mass spectrum, m/z (I_{rel} , %): 190 (2) [M^+], 189 (1), 117 (3), 101 (2), 87 (100), 73 (53).

General procedure for the synthesis of esters (8a, 8b). The mixture of 0.03 mol of dipentaerythritol formal, 0.03 mol of dry pyridine and 0.03 mol of chloroacetyl chloride was heated to 30°C for 1 h. The reaction mixture was kept in the fridge for 1 day, then poured into the mixture of 15 g of ice and 30 mL of 1 M HCl and stirred until the formation of suspension. The crude product was filtered and crystallized from isopropanol. The ratio **8a** : **8b** = 3 : 1.

Oxybis(methylene-1,3-dioxane-5,5-dimethylene)-bis-chloroacetate (8a). Mass spectrum, m/z , (I_{rel} , %): (276/278/280)/(3/1/0.4), (207/209)(30/10), 147 (31), (99/101)/(34/12), 83 (100), 55 (30).

Oxybis(methylene-1,3-dioxane-5,5-dimethylene)-bis-chloroacetate (8b). Mass spectrum, m/z , (I_{rel} , %):

276 (4), 278 (2), 280 (1), 207 (45), 209 (19), 147 (77), 99 (63), 101 (28), 83 (100), 55 (50).

General procedure for the synthesis of carbamates (10a, 10b). To the mixture of 0.05 mol of dipentaerythritol formal and 15 mL of hexane, 0.025 mol of phenylisocyanate in 5 mL of hexane was added and heated at stirring to 35°C. After completion of the reaction (TLC control) the mixture was cooled to room temperature, the formed crystals were filtered, washed with water, dried in the air and crystallized from isopropanol. Ratio **10a** : **10b** = 3 : 1. ¹H and ¹³C NMR spectral parameters of esters **10a**, **10b** are given in Table 2.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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