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PAPER

Intramolecular etherification of five-membered cyclic carbonates bearing hydroxyalkyl groups†

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We report a new one-pot synthetic route to tetrahydrofuran derivatives, which were unexpectedly produced under basic conditions by intramolecular etherification of substituted five-membered cyclic carbonates. For alcohols with vicinal hydroxyl groups, and additional OH groups at the β-position, intramolecular etherification leading to 3-hydroxytetrahydrofuran derivatives was observed. These reactions were studied for compounds having from 2 to 6 hydroxyl groups per molecule, and the mechanism was proposed. The developed method provides a new environmentally friendly approach to the synthesis of five-membered cyclic ether derivatives under non-acidic conditions.

Introduction

Cyclic carbonates are synthesized with the use of carbon dioxide – a cheap, easily available but environmentally burdensome starting material. They can be obtained almost directly from oxiranes and carbon dioxide, or indirectly in the reaction of vicinal diols with a "green monomer" – dimethyl carbonate. In combination with diamines biscyclic carbonates give way to the formation on non-isocyanate polyurethanes. However, cyclic carbonates bearing substituents containing free hydroxyl groups alone can be a source of many valuable compounds.

Cyclic ethers such as tetrahydrofuran are easily available from 1,4-diols by a cyclodehydration reaction carried out under acidic conditions.[1] However, when secondary and tertiary alcohols are used elimination and isomerization takes place besides the intramolecular etherification.

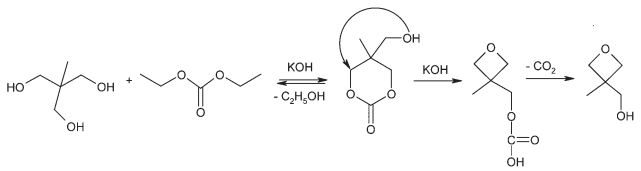
In the case of 1,4-diols containing an additional hydroxyl group at the 2-position or two OH groups at the 2-positions, 3,3-hydroxytetrahydrofuran or 3,4-dihydroxytetrafuran are produced, respectively. The synthesis of 3-hydroxytetrahydrofuran from (±)-1,2,4-butanetriol in the presence of *p*-toluenesulfonic acid monohydrate was described by Belleau and Au-Young.[2] Obtaining 3,4-dihydroxytetrahydrofuran from *meso*-erythritol carried out in the presence of trifluoromethanesulfonic acid[3] or *p*-toluenesulfonic acid was reported by Arceo *et al.*[4]

Isosorbide, a diol containing two fused THF rings, is industrially produced by dehydration of sorbitol using a strong acid catalyst.[5] Typical catalysts are sulfuric acid,[6] hydrochloric acid and phosphoric acid.[7] The disadvantages of the acid catalyzed reactions are equipment corrosion and high separation costs.[8] Recently, some solid acid catalysts based on zeolite or ion exchange resin have been developed and used in etherification processes.[9] Anhydro sugar alcohols find application as therapeutics, food additives, surfactants and in polymers synthesis.[10]

It is also known that four-membered cyclic ethers, oxetanes, can be easily obtained from the respective triols through six-membered cyclic carbonates *via* intramolecular etherification. 3-Methyl-3-hydroxymethyloxetane can be obtained in high yield (81%) in the reaction of 1,1,1-tris(hydroxymethyl)ethane with diethyl carbonate in the presence of basic catalyst (KOH).[11] The synthesis proceeds by intramolecular etherification of the six-membered cyclic carbonate with the methylol group (Scheme 1). According to the same reaction pathway, 3-ethyl-3-hydroxymethyloxetane was obtained from trimethylolpropane.[12]

As far as five-membered cyclic carbonate is concerned, depending on the catalyst and chemical structures of reagents, the reaction of alcohols with 1,3-dioxolan-2-ones can proceed according to two different mechanisms, in which after deprotonation alkoxy group attacks carbonyl carbon atom (reaction a) or alkyl carbon atom (reaction b) of the cyclic carbonate (Scheme 2).

The reaction (a) in which linear carbonate linkages are formed is reversible, whereas reaction (b), in which ether linkages are formed, is irreversible. As a consequence, even for a very low etherification reaction rate, after long reaction times the formation of ether derivatives is observed in relatively high yields.



Scheme 1 Synthesis of 3-methyl-3-hydroxymethyloxetane from 1,1,1-tris(hydroxymethyl)ethane and diethyl carbonate.[11]

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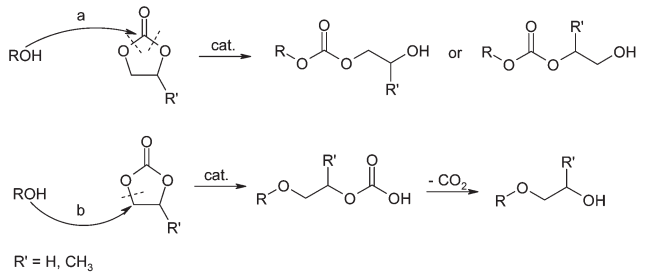
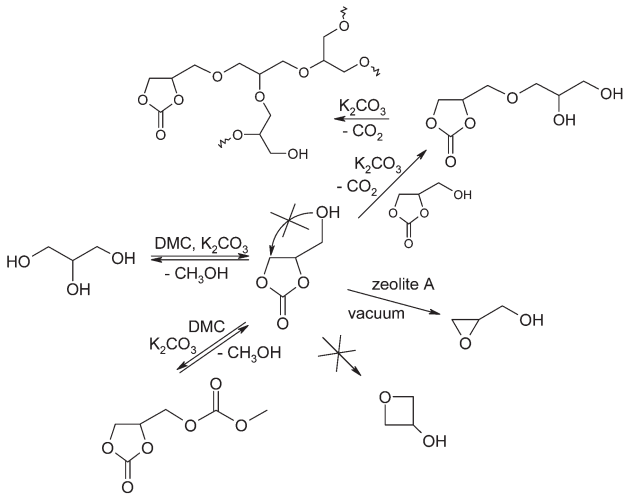


Scheme 2 Two reaction pathways of five-membered cyclic carbonates with alcohols.



Scheme 3 Synthesis of 5-hydroxymethyl-1,3-dioxolan-2-one and its derivatives in the reaction of glycerol with dimethyl carbonate in the presence of potassium carbonate.[14,15]

In our earlier work[13] it was reported that the presence of alkaline catalysts favors etherification. In the reaction of ethylene carbonate with 1,6-hexanediol at 140 °C in the presence of K_2CO_3 mainly oligo(oxyethylene)s were formed. On the other hand, the reaction carried out in the presence of a neutral catalyst such as NaCl led to oligo(hexamethylene carbonate)s with high selectivity. However, when the reaction temperature was increased (170 °C), a higher extent of etherification was observed again. It should be mentioned that the length of the diol hydrocarbon chain strongly influences etherification. For a shorter diol, such as 1,4-butanediol, even in the presence of NaCl at 145 °C the product containing 60% of oligo(oxyethylene) fragments was obtained. A similar effect was observed for diols containing heteroatoms such as oxygen and sulfur at the β-position in relation to the OH group and polyethers are formed almost selectively. When propylene carbonate was used instead of ethylene carbonate in the reaction with alcohols, etherification was dramatically suppressed. The steric effect and the presence of electron donating methyl groups in the 1,3-dioxolan-2-one ring directs the alkoxy group attacks selectively on the carbonyl carbon atom and only a small amount of ether units was present in the product. Thus, the reaction of 1,4-butanediol with propylene carbonate at 155 °C even in the presence of an alkaline catalyst such as K_2CO_3 proceeds with formation of mainly oligo(tetramethylene carbonate)s.[13]

In the case of alkyl substituted five-membered cyclic carbonates containing an OH group at the α-position in relation to the 1,3-dioxolan-2-one ring, no intramolecular etherification leading to 3-hydroxyoxetane was observed.[14] In the reaction of glycerol with dimethyl carbonate in the presence of K_2CO_3 carried out under mild conditions 5-hydroxymethyl-1,3-dioxolan-2-one is formed almost quantitatively (Scheme 3). At higher temperatures (>170 °C) intermolecular etherification takes place and hyperbranched polyglycerol is produced.[14] When the reaction was carried out at 180 °C under vacuum in the presence of zeolite A or γ-alumina catalyst, glycidol could be distilled off in a relatively high yield (86%).[15]

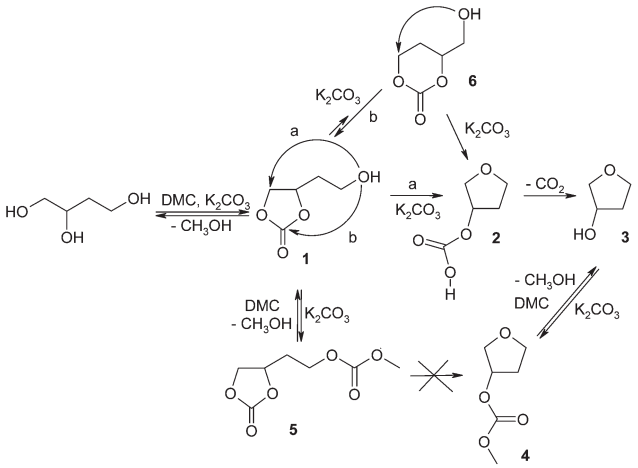
Five- and six-membered cyclic carbonates can be obtained according to two main synthetic routes. The first one is the addition reaction of carbon dioxide to cyclic ethers such as oxiranes[16] or oxetanes.[17] In the second method, 1,2- or 1,3-diols are used as starting materials in the reaction with phosgene or its derivatives (diphosgene or triphosgene).[18] Ariga *et al.*[19] developed a method for the synthesis of six-membered cyclic carbonates using ethyl chloroformate and triethylamine. The disadvantage of the latter two methods is the formation of a stoichiometric amount of triethylamine hydrochloride as a burdensome waste. Recently, instead of chlorine containing reagents, for the synthesis of five- and six-membered cyclic carbonates dimethyl carbonate (DMC) has been applied. DMC is a cheap and easily available "green" monomer produced on industrial scale, that makes the method based on DMC very convenient.[20]

Results and discussion

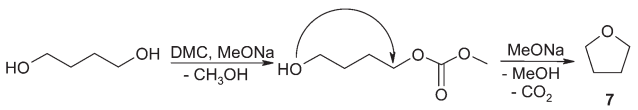
In the present study we have investigated the possibility of obtaining tetrahydrofuran derivatives containing additionally cyclic carbonate rings from substituted five-membered cyclic carbonates with hydroxyl groups at β-position in relation to the carbonate ring. The reaction mechanisms have been proposed and discussed, especially those for processes in which carbohydrates were used as starting materials.

It was found that substituted five-membered cyclic carbonate containing hydroxyl groups at β-position in relation to carbonate ring undergoes after longer time (21 h) intramolecular etherification in the presence of basic catalyst such as K_2CO_3 heated at 80 °C, and as a result 3-hydroxytetrahydrofuran (**3**) is formed as a main product. However, after short time (5 h) in the reaction of (±)-1,2,4-butanetriol with dimethyl carbonate the main product, depending on molar ratio of reagents, was 4-(2-hydroxyethyl)-1,3-dioxolan-2-one (**1**) or 4-(3,5-dioxa-4-oxyhexyl)-1,3-dioxolan-2-one (**5**) (Scheme 4). To obtain cyclic carbonate **1** in a high yield, the reaction should be carried out at the first stage under reflux without removing methanol from the reaction mixture.

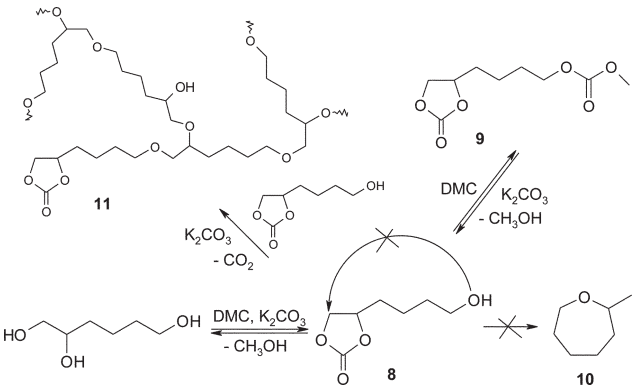
When (±)-1,2,4-butanetriol was reacted with dimethyl carbonate used in stoichiometric ratio at 80 °C in the presence of potassium carbonate, 4-(2-hydroxyethyl)-1,3-dioxolan-2-one (**1**) was obtained in high yield (93%) after 5 h. For higher excesses of DMC, butanetriol dicarbonate (**5**) was obtained. Under the same reaction conditions, but for longer reaction time (21 h) mainly 3-hydroxytetrahydrofuran (**3**) was obtained (Scheme 4).



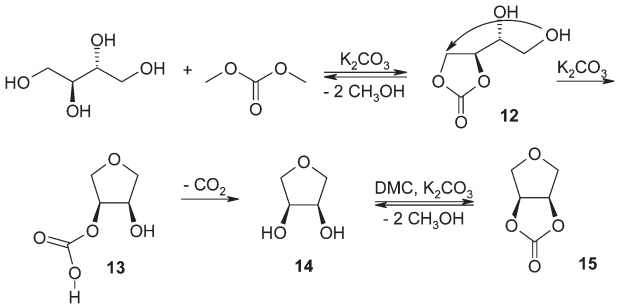
Scheme 4 Reaction of (±)-1,2,4-butanetriol with dimethyl carbonate in the presence of potassium carbonate.



Scheme 5 Reaction of 1,4-butanediol with dimethyl carbonate in the presence of sodium methoxide.



Scheme 6 Reaction of (±)-1,2,6-hexanetriol with dimethyl carbonate in the presence of potassium carbonate.



Scheme 7 Reaction of *meso*-erythritol with dimethyl carbonate in the presence of potassium carbonate.

It is worth mentioning that Ren and Liu[21] obtained **1** starting from (±)-1,2,4-butanetriol in a five step process, including the protection and deprotection strategy.

The five-membered cyclic ether **2** is produced according to the mechanism, in which the primary alkoxy group attacks the alkyl carbon atom in the 1,3-dioxolan-2-one ring (reaction a, Scheme 4) and as a result an unstable hydrocarbonate group is formed, which after decarboxylation is transformed into a hydroxyl group. This reaction is irreversible. The primary alkoxy group of **1** can also attack the carbonyl carbon atom of the cyclic carbonate (reaction b) leading to a less stable six-membered cyclic carbonate (**6**). Thus, taking into account that the latter reaction is reversible, more product of the irreversible reaction should be present in the reaction mixture after longer times. Moreover, the intramolecular etherification of 4-(hydroxymethyl)-1,3-dioxan-2-one (**6**) also leads to **3**. It was observed that a higher excess of DMC in the first step suppresses the formation of cyclic ether **3** (Scheme 4).

It should be mentioned that when 1,4-butanediol was used in the reaction with dimethyl carbonate (Scheme 5) a very small extent of intramolecular etherification was observed for the reaction carried out at 90 °C in the presence of basic catalyst such as K_2CO_3. The use of a much stronger base like sodium methoxide led to the formation of tetrahydrofuran (**7**) in much higher yield (48%, after 4 h at 90 °C) (Scheme 5).

In the case of alkyl substituted five-membered cyclic carbonate containing hydroxyl groups at the γ-position in relation to the carbonate ring, no intramolecular etherification under these conditions was observed. In the reaction of (±)-1,2,6-hexanetriol with DMC carried out at 80 °C in the presence of K_2CO_3, two products were obtained: 4-(4-hydroxybutyl)-1,3-dioxolan-2-one (**8**) (79%), and 4-(5,7-dioxa-6-oxyhexyl)-1,3-dioxolan-2-one (**9**) (67%), depending on the molar ratio of the reactants used. The seven-membered cyclic ether oxepan-2-ol (**10**) was not identified in the postreaction mixture (Scheme 6). Intramolecular etherification of **8** does not proceed due to the relatively small kinetic effect of the formation of unstable seven-membered cyclic ether – oxepan-2-ol (**10**). After long heating times, intermolecular etherification takes place and the branched polyether **11** is obtained.

It was observed by us that the presence of additional hydroxyl groups at the α-position in relation to the five-membered carbonate ring in 4-(hydroxymethyl)-1,3-dioxolan-2-one enhances intramolecular etherification and a tetrahydrofuran ring is produced even in the presence of a neutral catalyst and at relatively low reaction temperatures.

When *meso*-erythritol [(2*R*,3*S*)-butane-1,2,3,4-tetraol] containing four vicinal hydroxyl groups was reacted with dimethyl carbonate in stoichiometric ratio at 90 °C in the presence of K_2CO_3, (3*R*,4*S*)-3,4-dihydroxytetrahydrofuran (**14**) was obtained in high yield (86%) (Scheme 7).

It was found that at the reaction beginning, 4-(1,2-dihydroxyethyl)-1,3-dioxolan-2-one (**12**) is formed as an intermediate. In the FTIR spectrum of the intermediate an absorption band at 1789 cm^{-1}, which is characteristic for a carbonyl group of a five-membered cyclic carbonate can be observed. This absorption band disappeared after 12 h of heating at 90 °C (Fig. 1).

This reaction proceeds according to the same mechanism discussed for (±)-1,2,4-butanetriol. Moreover, the presence of

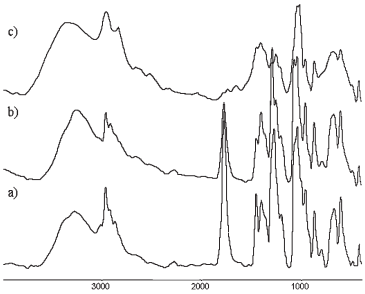


Fig. 1 FTIR (KBr) spectra of the intermediates of the reaction of *meso*-erythritol with stoichiometric molar ratio of dimethyl carbonate carried out at 90 °C in the presence of K_2CO_3 after: (a) 7 h, (b) 8 h, (c) 12 h.

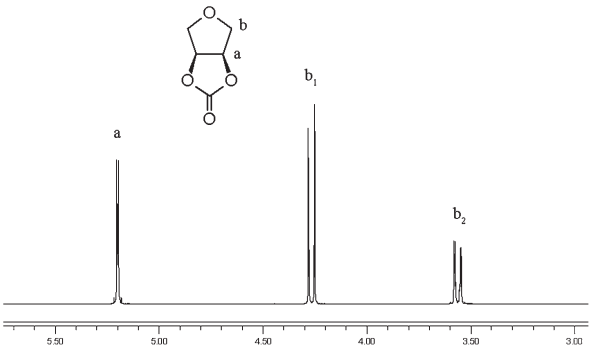


Fig. 2 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **15**.

an additional OH group enhances the attack on the alkyl carbon atom of the cyclic carbonate due to the formation of intramolecular hydrogen bonds with the carbonyl groups and the tetrahydrofuran derivative **14** if formed in a relatively short time.

It was found that when the reaction of *meso*-erythritol was carried out with molar excess of dimethyl carbonate under the same reaction conditions, (1*R*,5*S*)-2,4,7-trioxa-3-oxy-bicyclo [3.3.0]octane (**15**) a bicyclic derivative of tetrahydrofuran and 1,3-dioxolan-2-one was formed in high yield (Scheme 7). The product structure was confirmed by ^{1}H and ^{13}C NMR, HRMS, FTIR as well as X-ray crystallography. The methylene group protons appear as dd and ddd at 4.27 and 3.56 ppm, respectively. The methine group protons appear as a dd at 5.20 ppm (Fig. 2). In the ^{13}C NMR spectrum of **15** the signals corresponding to the methine and methylene carbon atoms are present at 79.99 and 72.94 ppm, respectively (Fig. S1†). The signal at 154.36 ppm can be assigned to a carbonyl carbon atom of cyclic carbonate. In the FTIR spectrum an absorption band corresponding to the carbonyl group of the five-membered cyclic carbonate (1793 cm^{-1}) was present and no absorption band of the hydroxyl group was observed.

The structure of compound **15** is depicted in Fig. 3 and selected bond lengths and angles are collected in Table S1.† It consists of two edge-sharing rings one of which adopts an envelope conformation – the tetrahydrofuran ring, and the other is flat – the carbonate ring. The angle between the mean ring planes equals 103.51(7)°. The carbonate ring is strained with C–O distances equal to 1.1969(16) Å for the terminal oxygen atom and

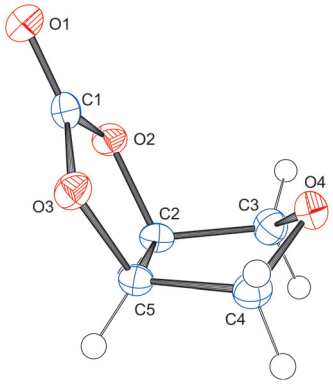
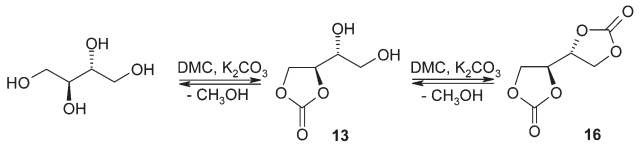


Fig. 3 ORTEP plot of the molecular structure of **15**. Thermal ellipsoids are drawn at 50% probability level.



Scheme 8 Synthesis of (4*R*,4′*S*)-4,4′-bi(1,3-dioxolane-2-one) (**16**) in the reaction of *meso*-erythritol with an excess of dimethyl carbonate in the presence of potassium carbonate at 70 °C.

1.3379(16)–1.3417(16) Å for the bridging oxygen atoms. These values are typical for five-membered carbonate rings retrieved from the Cambridge Structural Database (CSD)[22] – 1.191(8) Å and 1.342(11) Å for terminal and bridging oxygen atoms, respectively.[23] Individual molecules are connected in a 3D network *via* C–H···O hydrogen bonds. Double columns of molecules connected *via* hydrogen bridges involving tetrahydrofuran oxygen atoms and carbon atoms adjacent to them may be distinguished in the supramolecular organisation in the structure (C4–H4B···O4^{i} hydrogen bond, where i = −1/2 + *x*, 3/2 − *y*, 1 − *z*). Such columns, exhibiting the symmetry of $p2_1$ rod group, are in turn connected into a spatial structure *via* hydrogen bonds involving terminal oxygen atoms of the carbonate group (C4–H4A···O1^{ii} hydrogen bond, where ii = 1 − *x*, 1/2 + *y*, 1/2 − *z*).

As it was earlier found, lowering the reaction temperature reduces the extent of etherification. In the reaction of *meso*-erythritol with an excess of DMC carried out at 70 °C in the presence of K_2CO_3 biscyclic carbonate **16** can be obtained and isolated (Scheme 8). However, the yield of (4*R*,4′*S*)-4,4′-bi(1,3-dioxolane-2-one) (**16**) was rather low (5%). The structure of **16** was confirmed by ^{1}H and ^{13}C NMR, HRMS, and FTIR. The ^{1}H NMR spectrum of the biscyclic carbonate **16** is similar to that of (1*R*,5*S*)-2,4,7-trioxa-3-oxy-bicyclo[3.3.0]octane **15**. The methine group protons appear in the range of 5.16–5.10 ppm as a multiplet, but the methylene group protons appear at 4.60 and 4.39 ppm as two doublets of doublets (Fig. 4). In the ^{13}C NMR spectrum the signals corresponding to the methine and methylene carbon atom are present at 74.91 and 64.68 ppm, respectively. There is also one signal at 154.16 ppm, which is assigned to the carbonyl carbon atom of biscyclic carbonate (Fig. S2†). In the FTIR spectrum two absorption bands corresponding to the

carbonyl group of cyclic carbonate (1807 and 1783 cm^{-1}) were observed and no absorption band characteristic for the hydroxyl groups was found.

The application of ethylene carbonate instead of dimethyl carbonate and a neutral catalyst such as NaCl in the reaction with *meso*-erythritol led almost exclusively to (1*R*,5*S*)-2,4,7-trioxa-3-oxy-bicyclo[3.3.0]octane (**15**) (yield 96%), despite the lower reaction temperature (70 °C). The process was carried out with the use of toluene as an azeotrope-forming solvent removing ethylene glycol from the reaction system.

It was found that intramolecular etherification of cyclic carbonate can proceed also with secondary OH groups. However, in contrast to primary OH groups (*meso*-erythritol), this etherification needs longer reaction times or higher temperatures. Thus, D-sorbitol [(2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol] containing six vicinal hydroxyl groups in a molecule in the reaction with dimethyl carbonate carried out at 90 °C in the presence of K_2CO_3, produces (1*R*,4*S*,5*R*,6*R*)-6-(1,3-dioxolan-2-one-4-yl)-2,4,7-trioxa-3-oxy-bicyclo[3.3.0]octane (**20**) in 43% yield (Scheme 9). Increasing the reaction temperature (above 110 °C) in the presence of the same catalyst causes additional intramolecular etherification and isosorbide (**22**) as a final product is obtained (Scheme 9).

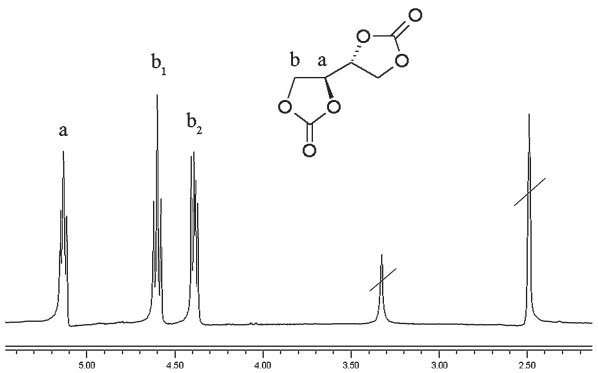
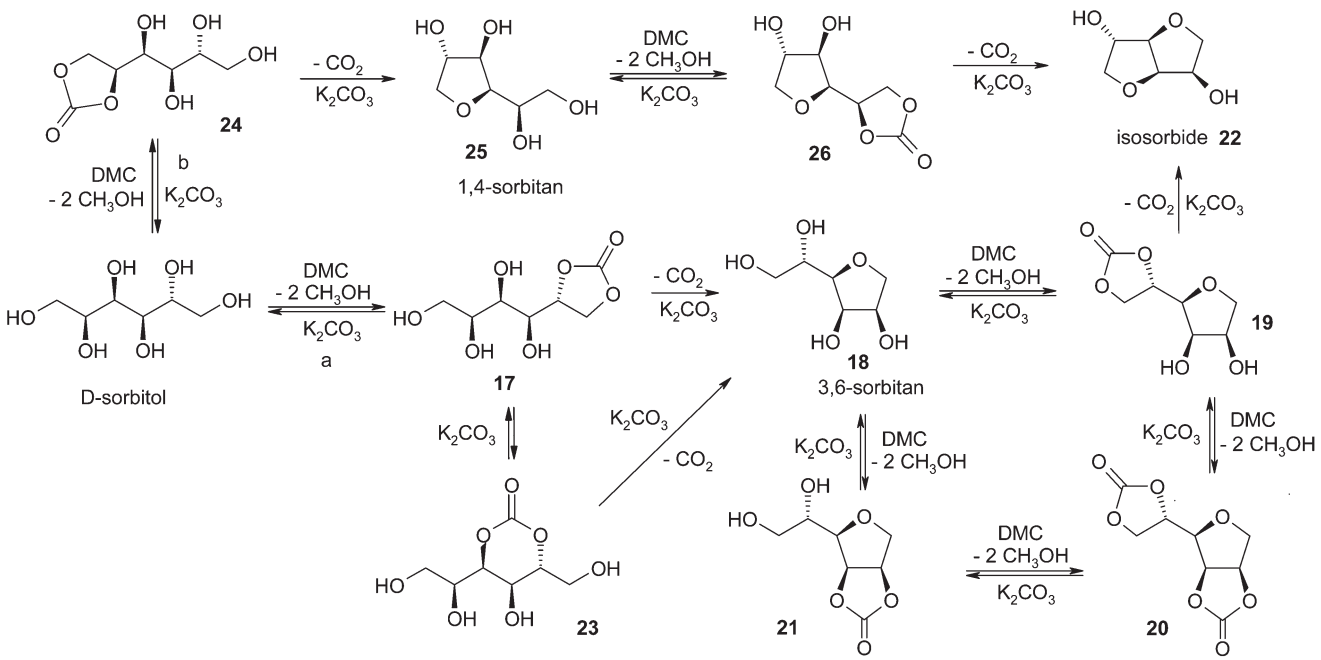


Fig. 4 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **16**.

The reaction of D-sorbitol with dimethyl carbonate in the presence of a basic catalyst can proceed according to two reaction pathways (Scheme 9). When the reaction started from primary hydroxyl group at position 6, 4-(1,2,3,4-tetrahydroxybutyl)-1,3-dioxolan-2-one (**17**) is formed (pathway a) as an intermediate. Then, as a result of the attack of the secondary alkoxy group on the methylene group of cyclic carbonate, followed by decarboxylation, 3,6-sorbitan [(3*S*)-2-(1,2-dihydroxyethyl)-3,4-dihydroxytetrahydrofuran] (**18**) is produced (Scheme 9). It should be added that similarly to the reaction of DMC with *meso*-erythritol, six-membered cyclic carbonate **23** can be formed as an intermediate. Moreover, in this case six-membered cyclic carbonate containing alkyl substituents at positions 4 and 6 are more stable as was observed by Rokicki *et al.*[24] and Hatano *et al.*[1]

At the next step, under an excess of DMC, the intermediate with a five-membered cyclic carbonate (**19**) is formed. The intermediate **19** is transformed into (1*R*,4*S*,5*R*,6*R*)-6-(1,3-dioxolan-2-one-4-yl)-2,4,7-trioxa-3-oxy-bicyclo[3.3.0]octane (**20**) in the reaction with an excess of DMC or by intramolecular etherification into isosorbide (**22**). Higher temperatures (>110 °C) enhance the etherification. (1*R*,4*S*,5*R*,6*R*)-6-(1,3-Dioxolan-2-one-4-yl)-2,4,7-trioxa-3-oxy-bicyclo[3.3.0]octane, due to high melting point (215–216 °C) can be easily purified by recrystallization from acetonitrile. The structure of **20** was confirmed by ^{1}H and ^{13}C NMR (Fig. 5 and S3†), HRMS, FTIR, as well as X-ray crystallography. In the FTIR spectrum two absorption bands corresponding to the carbonyl group of different cyclic carbonates (1806 and 1777 cm^{-1}) were observed and no absorption band of the hydroxyl group was found.



Scheme 9 Reaction of D-sorbitol with dimethyl carbonate carried out in the presence of potassium carbonate.

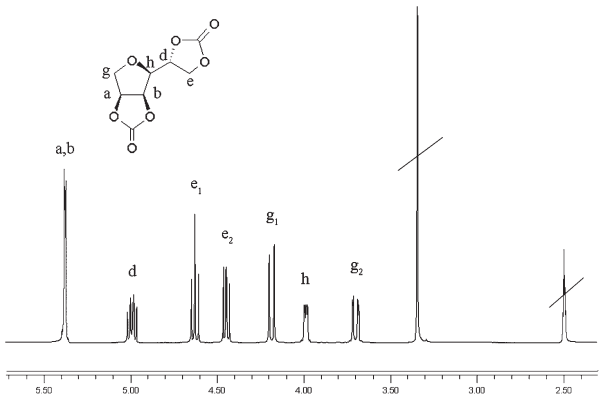


Fig. 5 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **20**.

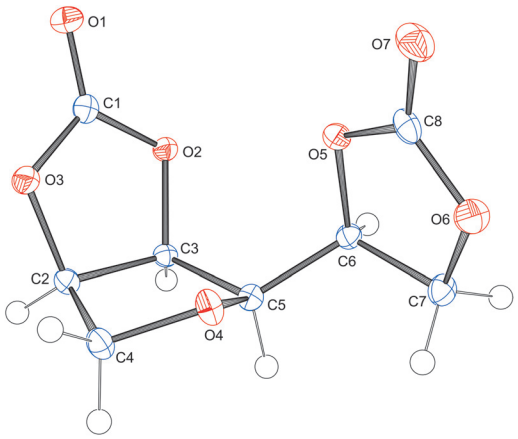


Fig. 6 ORTEP plot of the molecular structure of **20**. Thermal ellipsoids are drawn at 50% probability level.

When the reaction of D-sorbitol with DMC starts from the OH group at position 1 (reaction pathway b, Scheme 9) 1,4-sorbitan [(3*S*)-2-(1,2-dihydroxyethyl)-3,4-dihydroxytetrahydrofuran] (**25**) as the intermediate is produced. As it can be noticed in this tetrahydrofuran derivative, two hydroxyl groups are in *trans* configuration and biscyclic carbonate like **20** can not be formed due to the high stress of the potential five-membered carbonate ring. The final product, isosorbide (**22**), is produced according to both reaction pathways.

Selected geometrical parameters of **20** determined from X-ray crystal study are given in Table S3.† The molecule of compound **20**, presented in Fig. 6, can be derived from the molecule of compound **15** by substituting the H3B hydrogen with a flat ring of ethylene glycol carbonate. The C–O bond lengths in the carbonate groups are typical for systems containing five-membered carbonate rings. They are equal to 1.1972(19) Å and 1.202(2) Å for terminal oxygen atoms and range from 1.333(2) to 1.3411 (19) Å for the bridging ones. The angle between mean ring planes of the fused carbonate and tetrahydrofuran rings is slightly larger than in compound **15** and equals 107.29(9)°, whereas the C3C5C6O5 dihedral angle, describing the mutual orientation of the other carbonate ring and the tetrahydrofuran ring amounts to 68.74(18)°. The tetrahydrofuran ring adopts an envelope conformation. Interestingly, the supramolecular organisation of molecules in the crystal structure of **20** is analogous to that present in compound **15** even though a bulky substituent was introduced into compound **20**. Neighbouring molecules related by a 2_1 screw axis are connected *via* C–H···O hydrogen bonds into columns, which are in turn linked with one another in a 3D network.

Experimental

Materials

(±)-1,2,4-Butanetriol (BDH Laboratory Reagent), (±)-1,2,6-hexanetriol (Koch–Light Laboratories LTD), (2*R*,3*S*)-butane-1,2,3,4-tetraol (Sigma), sodium methoxide, dimethyl carbonate (Sigma-Aldrich), ethylene carbonate (Aldrich), D-sorbitol, potassium carbonate, sodium chloride, anhydrous magnesium sulfate, hydrochloric acid, 1,4-dioxane, dichloromethane, toluene, tetrahydrofuran, acetone, acetonitrile, ethyl acetate, hexane (Polish Chemical Reagents, Gliwice) were used as received.

Measurements

IR spectra were recorded on a Biorad FTIR spectrometer (KBr pellets). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR 400 MHz spectrometer. The two-dimensional NMR spectra were recorded on Varian VNMRS 600 MHz spectrometer. Chemical shifts are reported in δ units and coupling constants are reported in Hz. Deuterated solvents were used and tetramethylsilane served as internal standard. High-resolution (HR) electrospray ionisation (ESI) mass spectra were recorded on a LCMS IT-TOF instrument. Optical rotation was measured at the sodium line at ambient temperature in acetonitrile solution. Single crystals of **15** and **20** were grown from dichloromethane–hexane mixture and acetonitrile, respectively. Suitable monocrystals were selected under a polarizing microscope, mounted in inert oil (Immersion Oil type A, Cargill) and transferred to the cold gas stream of the diffractometer. Diffraction data were measured on the Agilent κ-CCD Gemini A Ultra diffractometer at 100(2) K with mirror-focused Cu-Kα radiation for **15** and with graphite-monochromated Mo-Kα radiation for **20**. Cell refinement and data collection as well as data reduction and analysis were performed with the CrysAlis^{PRO} software.[25] The structures were solved by direct methods and subsequent Fourier-difference synthesis with SHELXS-97 and refined by full-matrix least-squares against F^2 with SHELXL-97[26] within the OLEX2 program suite.[27] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms except for H2, H5 in compound **15**, H2 and H3 in compound **20** were introduced at calculated positions and refined as riding atoms with isotropic displacement parameters equal to 1.2 times that of the parent atoms. In case of compound **20** the absolute structure was not determined basing on diffraction experiment and the absolute configuration was assigned to agree with that of the molecule's precursor. Data were analysed using OLEX2 and PLATON.[28] Fig. 3 and 6 were created using ORTEP-3 for Windows.[29] Crystal data and structure refinement parameters are given in Table S3.†

Synthesis of 4-(2-hydroxyethyl)-1,3-dioxolan-2-one (1)

In a 25 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 1.36 g (0.0128 mol) of (±)-1,2,4-butanetriol, 1.15 g (0.0128 mol) of dimethyl carbonate, and 0.02 g (0.14 mmol) of potassium carbonate were placed. The reaction was carried out at 80 °C, and the reaction progress was monitored by TLC. After the disappearance of the starting material, methanol was distilled off under reduced pressure. Then, the residue was washed with 3% HCl, water and extracted with ethyl acetate (3 × 30 cm^3). The combined organic phases were dried by anhydrous magnesium sulfate, and evaporated to dryness. The product was purified by column chromatography (silica gel, ethyl acetate). 1.34 g of **1** as colorless liquid (yield 79%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): 4.97–4.88 (m, 1H, $CH_{cyc.}$), 4.59 (dd, 1H, $CH_{2cyc.}$, J_1 = 7.9Hz, J_2 = 8.5 Hz), 4.19 (dd, 1H, $CH_{2cyc.}$, J_1 = 7.5 Hz, J_2 = 8.6 Hz), 3.87–3.74 (m, 2H, CH_2OH), 2.24 (bs, 1H, OH), 2.09–1.91 (m, 1H, CH_2CH_2OH). ^{13}C NMR (400 MHz, $CDCl_3$): 155.03 (C═O), 75.03 ($CH_{cyc.}$), 69.68 ($CH_{2cyc.}$), 57.85 (CH_2OH), 35.85 (CH_2CH_2OH). FTIR (KBr): 3400 (OH), 2959–2892 (C–H), 1790 (C═O), 1182–1064 (C–O), 777 (carbonate ring).

Synthesis of 3-hydroxytetrahydrofuran (3)[2]

In a 25 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 5.01 g (0.0472 mol) of (±)-1,2,4-butanetriol, 4.25 g (0.0472 mol) of dimethyl carbonate, and 0.06 g (4.35 mmol) of potassium carbonate were placed. Reaction was carried out at 80 °C, and the reaction progress was monitored by FTIR spectroscopy until complete decay of the absorption band corresponding to carbonyl groups. Then, methanol was distilled off under reduced pressure. The product was purified by vacuum distillation (111–112 °C, 4 mmHg) to afford **3** as a colorless liquid (yield 93%). ^{1}H NMR (400 MHz, $CDCl_3$): 4.39 (ddt, 1H, CHOH, J_1 = 1.9 Hz, J_2 = 3.8 Hz, J_3 = 5.7 Hz), 3.88 (dt, 1H, CH_2CH_2O, J_1 = 7.0 Hz, J_2 = 8.5 Hz), 3.74 (dt, 1H, CH_2CH_2O, J_1 = 4.1 Hz, J_2 = 8.5 Hz), 3.69 (dd, 1H, $CHCH_2O$, J_1 = 3.9 Hz, J_2 = 9.7 Hz), 3.65 (ddd, 1H, $CHCH_2O$, J_1 = 1.9 Hz, J_2 = 9.7 Hz, J_3 = 1.0 Hz), 1.99 (ddt, 1H, CH_2CH_2O, J_1 = 5.7 Hz, J_2 = 8.7 Hz, J_3 = 13.3 Hz), 1.82 (m, 1H, CH_2CH_2O). ^{13}C NMR (400 MHz, $CDCl_3$): 75.24 ($CHCH_2O$), 71.38 (CHOH), 66.57 (CH_2CH_2O), 35.14 (CH_2CH_2O). FTIR (KBr): ν = 3401 (O–H), 2951–2876 (C–H), 1122–1048 (C–O). Analysis of the isolated product was consistent with that reported in the reference.

Synthesis of 4-(3,5-dioxa-4-oxyhexyl)-1,3-dioxolan-2-one (5)

In a 50 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 2.73 g (0.0257 mol) of (±)-1,2,4-butanetriol, 23.17 g (0.2572 mol) of dimethyl carbonate, and 0.03 g (2.17 mmol) of potassium carbonate were placed. The reaction was carried out at 80 °C, and the reaction progress was monitored by TLC, and by FTIR spectroscopy until complete decay of the absorption band corresponding to hydroxyl groups. Then, methanol and the excess of dimethyl carbonate were distilled off under reduced pressure. The product was purified by vacuum distillation (59–60 °C, 1 mbar). 3.38 g of **2** as a light yellow liquid (yield 67%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): 4.91–4.82 (m, 1H, $CH_{cyc.}$), 4.59 (dd, 1H, $CH_{2cyc.}$, J_1 = 8.0 Hz, J_2 = 8.5 Hz), 4.38–4.23 (m, 2H, $CH_2OC(O)O$), 4.14 (dd, 1H, $CH_{2cyc.}$, J_1 = 7.3 Hz, J_2 = 8.6 Hz), 3.79 (s, 3H, CH_3), 2.21–2.07 (m, 2H, CH_2CH_2O). ^{13}C NMR (400 MHz, $CDCl_3$): 155.43 ($C{=}O_{cyc.}$), 154.74 ($C{=}O_{lin.}$), 74.16 ($CH_{cyc.}$), 69.45 ($CH_{2cyc.}$), 63.75 ($CH_2OC(O)O$), 55.29 (CH_3), 33.31 ($CHCH_2$). FTIR (KBr): 2962–2873 (C–H), 1803 ($C{=}O_{cyc.}$), 1749 ($C{=}O_{lin.}$), 1284–1264 (C–O), 1174–1063 (C–O), 792 (linear carbonate), 774 (carbonate ring).

Synthesis of 4-(4-hydroxybutyl)-1,3-dioxolan-2-one (8)[30]

In a 25 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 2.55 g (0.0190 mol) of (±)-1,2,6-hexanetriol, 1.71 g (0.0189 mol) of dimethyl carbonate, and 0.03 g (2.17 mmol) of potassium carbonate were placed. The reaction was carried out at 80 °C, and the reaction progress was monitored by TLC. After the disappearance of the starting material, methanol was distilled off under reduced pressure. Then, the residue was washed with 3% HCl, water and extracted with dichloromethane (3 × 30 cm^3). The combined organic phases were dried with anhydrous magnesium sulfate, and evaporated to dryness. The product was purified by column chromatography (silica gel, tetrahydrofuran). 1.86 g of **8** as a colorless liquid (yield 61%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): 4.76–4.66 (m, 1H, $CH_{cyc.}$), 4.53 (t, 1H, $CH_{2cyc.}$, J = 8.2 Hz), 4.14 (t, 1H, OH, J = 6.3 Hz), 4.07 (dd, 1H, $CH_{2cyc.}$, J_1 = 7.2 Hz, J_2 = 8.5 Hz), 3.65 (t, 2H, CH_2OH, J = 6.1 Hz), 1.88–1.78 (m, 1H, CH_2CH), 1.78–1.67 (m, 3H, CH_2CH + CH_2CH_2OH), 1.65–1.54 (m, 1H, CH_2CH_2CH), 1.54–1.41 (m, 1H, CH_2CH_2CH). ^{13}C NMR (400 MHz, $CDCl_3$): 155.69 ($C{=}O_{cyc.}$), 69.29 ($CH_{cyc.}$), 67.25 ($CH_{2cyc.}$), 62.14 (CH_2OH), 33.57 (CH_2CH), 28.10 (CH_2CH_2OH), 20.80 (CH_2CH_2CH). FTIR (KBr): 3528 (O–H), 2945–2870 (C–H), 1791 ($C{=}O_{cyc.}$), 1268 (C–O), 1173–1063 (C–O), 776 (carbonate ring).

Synthesis of 4-(5,7-dioxa-6-oxyoctyl)-1,3-dioxolan-2-one (9)[1]

In a 150 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 13.09 g (0.0976 mol) of (±)-1,2,6-hexanetriol, 87.90 g (0.9758 mol) of dimethyl carbonate, and 0.13 g (9.42 mmol) of potassium carbonate were placed. The reaction was carried out at 80 °C, and the reaction progress was monitored by TLC, and by FTIR spectroscopy until complete decay of the absorption band corresponding to hydroxyl groups. Then, methanol and the excess of dimethyl carbonate were distilled off under reduced pressure. Then, the residue was washed with 3% HCl, water and extracted with dichloromethane (3 × 50 cm^3). The combined organic phases were dried with anhydrous magnesium sulfate, and evaporated to dryness. 17.44 g of **9** as a light yellow liquid (yield 82%) were obtained. ^{1}H NMR (400 MHz, $CDCl_3$): 4.67–4.59 (m, 1H, $CH_{cyc.}$), 4.45 (t, 1H, $CH_{2cyc.}$, J = 8.2 Hz), 4.04 (t, 2H, $CH_2OC(O)O$), J = 6.4 Hz), 3.98 (dd, 1H, $CH_{2cyc.}$, J_1 = 7.2 Hz, J_2 = 8.5 Hz), 3.66 (s, CH_3, 1H), 1.78–1.67 (m, 1H, CH_2CH), 1.67–1.57 (m, 3H, CH_2CH + CH_2CH_2O), 1.54–1.42 (m, 1H, CH_2CH_2CH), 1.42–1.31 (m, 1H, CH_2CH_2CH). ^{13}C NMR (400 MHz, $CDCl_3$): 155.68 ($C{=}O_{cyc.}$),

154.85 (C═$O_{lin.}$), 69.20 ($CH_{cyc.}$), 67.30 ($CH_{2cyc.}$), 67.30 ($CH_2OC(O)O$), 54.72 (CH_3), 33.31 (CH_2CH), 28.11 ($CH_2CH_2OC(O)O$), 20.93 (CH_2CH_2CH). FTIR (KBr): 2960–2872 (C–H), 1800 (C═$O_{cyc.}$), 1749 (C═$O_{lin.}$), 1265 (C–O), 1171–1065 (C–O), 794 (linear carbonate), 776 (carbonate ring). Analysis of the isolated product was consistent with that reported in the reference.

Synthesis of (3*R*,4*S*)-3,4-dihydroxytetrahydrofuran (14)[3]

In a 100 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 8.80 g (0.0721 mol) of (2*R*,3*S*)-butane-1,2,3,4-tetraol, 6.49 g (0.0720 mol) of dimethyl carbonate, 0.10 g (7.25 mmol) of potassium carbonate, and 40 cm^3 of 1,4-dioxane were placed. The reaction was carried out at 90 °C, and the reaction progress was monitored by FTIR spectroscopy until complete decay of the absorption band corresponding to carboxyl group. Then, methanol and 1,4-dioxane were distilled off under reduced pressure. The product was purified by vacuum distillation (102–103 °C, 2 mmHg) to afford **14** as a colorless viscous oil (86%). ^{1}H NMR (400 MHz, $CDCl_3$): 4.24 (m, 2H, C*H*OH), 3.89 (dd, 2H, CH_2O, J_1 = 5.2 Hz, J_2 = 9.6 Hz), 3.72 (dd, 2H, CH_2O, J_1 = 3.4 Hz, J_2 = 9.6 Hz), 3.68 (bs, 2H, OH). ^{13}C NMR (400 MHz, $CDCl_3$): 72.82 (CH_2O), 71.30 (CHOH). FTIR (KBr): ν = 3400 (O–H), 2950–2880 (C–H), 1129–1057 (C–O). Analysis of the isolated product was consistent with that reported in the reference.

Synthesis of (1*R*,5*S*)-2,4,7-trioxa-3-oxybicyclo[3.3.0]octane (15) – variant A

In a 150 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 9.89 g (0.0810 mol) of (2*R*,3*S*)-butane-1,2,3,4-tetraol, 73.02 g (0.8106 mol) of dimethyl carbonate, 0.12 g (8.69 mmol) of potassium carbonate, and 30 cm^3 of 1,4-dioxane were placed. The reaction was carried out at 90 °C, and the reaction progress was monitored by FTIR spectroscopy until complete decay of the absorption band corresponding to hydroxyl groups. Then, methanol, 1,4-dioxane, and the excess of dimethyl carbonate were distilled off under reduced pressure. The residue was washed with 3% HCl, and water. Dichloromethane was added in five 50 cm^3 portions in order to collect the product. Combined organic phases were dried with anhydrous magnesium sulfate, and left for crystallization. The crystalline product was purified by recrystallization from dichloromethane. 7.9 g of **15** (yield 74%) were obtained. Mp 76.0–77.5 °C. HRMS for $C_5H_6O_4$: calculated $[M + Na]^+$ = 153.0158 g mol^{-1}, found $[M + Na]^+$ = 153.0152 g mol^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 5.19 (dd, 2H, CH, J_1 = 1.2 Hz, J_2 = 2.1 Hz), 4.24 (dd, 2H, CH_2, J_1 = 1.2 Hz, J_2 = 11.2 Hz), 3.55 (ddd, 2H, CH_2, J_1 = 1.2 Hz, J_2 = 2.2 Hz, J_3 = 12.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): 154.36 (C═O), 79.99 (CHOC(O)O), 72.30 (CH_2O). FTIR (KBr): 2949–2874 (C–H), 1793 (C═O), 1168–1111 (C–O), 1092–1050 (C–O), 772 (carbonate ring).

Synthesis of (1*R*,5*S*)-2,4,7-trioxa-3-oxy-bicyclo[3.3.0]octane (15) – variant B

In a 250 cm^3 three-neck flask equipped with a magnetic stirrer, thermometer, Dean–Stark receiver, condenser, and a gas inlet, 10.32 g (0.0845 mol) of (2*R*,3*S*)-butane-1,2,3,4-tetraol, 22.32 g (0.2536 mol) of ethylene carbonate, 0.15 g (2.57 mmol) of sodium chloride, and 80 cm^3 of toluene were placed. The reaction was carried out at 70 °C under reduced pressure (180 Tr), collecting ethylene glycol in a Dean–Stark receiver. When the glycol was collected, the azeotropic solvent evaporated under vacuum. The product was purified by column chromatography (silica gel, ethyl acetate). 10.55 g of **15** (yield 96%) were obtained. Mp. 76–77.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 5.20 (dd, 2H, CH, J_1 = 1.2 Hz, J_2 = 2.1 Hz), 4.26 (dd, 2H, CH_2, J_1 = 1.4 Hz, J_2 = 11.0 Hz), 3.56 (ddd, 2H, CH_2, J_1 = 1.2 Hz, J_2 = 2.3 Hz, J_3 = 12.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): 154.36 (C═O), 79.99 (CHOC(O)O), 72.30 (CH_2O). FTIR (KBr): 2964–2871 (C–H), 1793 (C═O), 1167–1110 (C–O), 1093–1049 (C–O), 771 (carbonate ring).

Synthesis of (4*R*,4′*S*)-4,4′-bi(1,3-dioxolane-2-one) (16)

In a 250 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 11.87 (0.0972 mol) of (2*R*,3*S*)-butane-1,2,3,4-tetraol, 87.56 g (0.9720 mol) of dimethyl carbonate, 0.13 g (9.42 mmol) of potassium carbonate, and 40 cm^3 of tetrahydrofuran were placed. The reaction was carried out at 70 °C, and the reaction progress was monitored by TLC, and by FTIR spectroscopy observing the changes of the signals derived from the cyclic carbonate carbonyl group and hydroxyl groups. Then, methanol, tetrahydrofuran, and the excess of dimethyl carbonate were distilled off under reduced pressure. The residue was taken up in dichloromethane, and the precipitated product was filtered off. Recrystallization from acetone yielded 5% of **16**. Mp. 170–172 °C. HRMS for $C_6H_6O_6$: calculated $[M + Na]^+$ = 197.0057 g mol^{-1}, found $[M + Na]^+$ = 197.0049 g mol^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 5.16–5.10 (m, 2H, CH), 4.60 (dd, 2H, CH_2, J_1 = 8.6 Hz, J_2 = = 9.1 Hz), 4.39 (dd, 2H, CH_2, J_1 = 5.8 Hz, J_2 = 9.1 Hz). ^{13}C NMR (400 MHz, DMSO-d_6): 154.16 (C═O), 74.91 (CH), 64.68 (CH_2). FTIR (KBr): 2968–2862 (C–H), 1810 (C═O), 1785 (C═O), 1145–1083 (C–O), 771 (carbonate ring).

Synthesis of (1*R*,4*S*,5*R*,6*R*)-6-(1,3-dioxolan-2-one-4-yl)-2,4,7-trioxa-3-oxy-bicyclo[3.3.0]octane (20)

In a 50 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 2.89 g (0.0159 mol) of D-sorbitol, 14.29 g (0.1586 mol) of dimethyl carbonate, 20 cm^3 of 1,4-dioxane, and 0.02 g (0.145 mmol) of potassium carbonate were placed. The reaction was carried out at 80 °C, and the reaction progress was monitored by TLC, and by FTIR spectroscopy until complete decay of the absorption band corresponding to hydroxyl groups. Then, it was cooled down and the obtained precipitate was filtrated off. The product was purified by recrystallization from acetonitrile. 1.48 g of **20** (yield 43%) was obtained. Mp. 215–216 °C, $[\alpha]_D$ −3 (*c*, 0.4, acetonitrile). HRMS for $C_8H_8O_7$: calculated $[M + Na]^+$ = 239.0162 g mol^{-1}, found

$[M + Na]^+$ = 239.0172 g mol^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 5.38–5.36 (m, 2H, C*H*OC(O)O$_{biscyc.}$), 4.99 (ddd, 1H, CH$_{cyc.}$, J_1 = 5.5 Hz, J_2 = 6.4 Hz, J_3 = 8.7 Hz), 4.62 (dd, 1H, CH$_{2cyc.}$, J_1 = 8.6 Hz, J_2 = 8.6 Hz), 4.44 (dd, 1H, CH$_{2cyc.}$, J_1 = 8.5 Hz, J_2 = 6.5 Hz), 4.18 (d, 1H, CH$_{2biscyc.}$, J = 12.0 Hz), 3.98 (dd, 1H, CHO$_{biscyc.}$, J_1 = 2.2 Hz, J_2 = 5.4/Hz), 3.69 (m, 1H, CH$_{2biscyc.}$). ^{13}C NMR (400 MHz, DMSO-d_6): 144.95 (C═O$_{cyc.}$), 144.22 (C═O$_{cyc.}$), 71.41 (CHO$_{biscyc.}$), 71.10 (CH$_{cyc.}$), 69.92 (OCH$_2$*C*HOC(O)O$_{biscyc.}$), 64.35 (OCH*C*HOC(O)O$_{biscyc.}$), 62.11 (CH$_{2biscyc.}$), 56.63 (CH$_{2cyc.}$). FTIR (KBr): 2985–2882 (C–H), 1806 (C═O$_{cyc.}$), 1777 (C═O$_{cyc.}$), 1193–1178 (C–O), 774 (carbonate ring).

Synthesis of isosorbide (22)[31]

In a 100 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 3.15 g (0.0173 mol) of D-sorbitol, 15.58 g (0.1729 mol) of dimethyl carbonate, 20 cm^3 of 1,4-dioxane, and 0.02 g (0.145 mmol) of potassium carbonate were placed. The reaction was carried out at 90 °C, and the reaction progress was monitored by TLC. Then, methanol, 1,4-dioxane and excess of dimethyl carbonate were distilled off and the reaction temperature was increased to 120 °C. At this temperature intense carbon dioxide liberation was observed. The product was purified by vacuum distillation (126–127 °C, 1 mmHg). 1.07 g of **22** (yield 42%) was obtained. Mp. 61–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 4.64 (t, 1H, CHO, J = 4.9 Hz), 4.40–4.33 (m, 2H, CHO + C*H*OH), 4.29 (dd, 1H, C*H*OH, J_1 = 5.7 Hz, J_2 = 11.4 Hz), 3.97 (d, 1H, CH$_2$, J = 10.0 Hz), 3.92–3.82 (m, 2H, CH$_2$,), 3.54 (dd, 1H, CH$_2$, J_1 = 5.8 Hz, J_2 = 9.4 Hz), 3.05–2.55 (bs, 2H, OH). ^{13}C NMR (400 MHz, $CDCl_3$): 88.25 (CHO), 81.80 (CHO), 76.65 (CHOH), 75.90 (CH$_2$), 73.64 (CHOH), 72.43 (CH$_2$). FTIR (KBr): 3383 (O–H), 2948–2877 (C–H), 1123–1046 (C–O). Analysis of the isolated product was consistent with that reported in the reference.

Synthesis of tetrahydrofuran

In a 25 cm^3 three-neck flask equipped with a magnetic stirrer, condenser and thermometer, 0.99 g (0.011 mol) of 1,4-butanediol, 3.02 g (0.0335 mol) of dimethyl carbonate, and 1.85 g (0.0342 mol) of sodium alkoxide, and 6 cm^3 of 1,4-dioxane were placed. The reaction was carried out at 90 °C, and the reaction progress was monitored by gas chromatography. Then, methanol, 1,4-dioxane, excess of dimethyl carbonate, and tetrahydrofuran were distilled off under reduced pressure. The distillate was analyzed by gas chromatography. Tetrahydrofuran was obtained in 48% yield.

Conclusions

Diols with vicinal hydroxyl groups easily form five-membered cyclic carbonates in high yields in the reaction with dimethyl carbonate in the presence of an alkaline catalyst such as K_2CO_3. However, compounds with an additional OH group at the β-position in relation to the vicinal OH groups after longer reaction times while undergoing the same reaction conditions causes intramolecular etherification resulting in 3-hydroxytetrahydrofuran derivatives. In case of compounds with four vicinal hydroxyl groups it is difficult to obtain biscyclic carbonates in the reaction with DMC, even for the reaction carried out at a lower temperature and in the presence of neutral catalyst. The presented synthetic pathway represents an environmentally friendly approach to the synthesis of five-membered cyclic ether derivatives under non-acidic conditions. The biscyclic carbonates containing the tetrahydrofuran ring can be used in the synthesis of biodegradable non-isocyanate polyurethanes.

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