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Methylation and Carboxymethylation of Oxyalkyl-1,3-dioxacycloalkanes with Dimethyl Carbonate Catalyzed by $W(CO)_6$ and $Mn_2(CO)_{10}$

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Abstract—$W(CO)_6$-catalyzed condensation of 2,2-dimethyl-1,4-oxymethyl-1,3-dioxolane with dimethyl carbonate has resulted in selective formation of methyl ester of the starting heterocyclic alcohol. $Mn_2(CO)_{10}$ has catalyzed oxymethyl-1,3-dioxacycloalkane transformation into the corresponding non-symmetrical and symmetrical carbonates; selectivity of the process is determined by the alcohol-to-dimethyl carbonate molar ratio. A mixture of 5- and 6-mer formals of glycerol and 1,2,4-butanetriol has selectively reacted with dimethyl carbonate in the presence of $Mn_2(CO)_{10}$ to form a mixture of the corresponding non-symmetrical carbonates.

Keywords: dialkyl carbonate, catalyst, oxyalkyl-1,3-dioxacycloalkanes, ether, ester, metal carbonyl

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Conversion of triols (glycerol, 1,1,1-trioxymethylalkanes, etc.) into isopropylidene derivatives followed by functionalization of hydroxymethylene moiety is a general approach used in fine organic synthesis [1–3]. However, preparation of ethers and esters of hydroxylmethyl-1,3-dioxacycloalkanes via this procedure is accompanied by rapid heterocycle degradation under conditions of acid catalysis, reducing the desired product yield and the process selectivity [4].

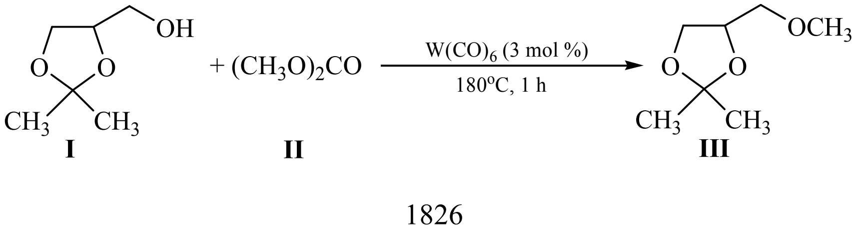
It has been recently shown that interaction of alcohols with dimethyl carbonate in the presence of W, Mn, V-, and Co-containing complex catalysts affords the corresponding ethers and esters with high selectivity [5].

We explored the application of that reaction for esterification of hydroxyalkyl-1,3-dioxacycloalkanes. It was found that heating (180°C) of 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane **I** with dimethyl carbonate **II** in the presence of tungsten hexacarbonyl led to the formation of methyl ether **III** with selectivity of 100% (conversion of the alcohol was of 50%). No esters were formed in the presence of that catalyst (Scheme 1).

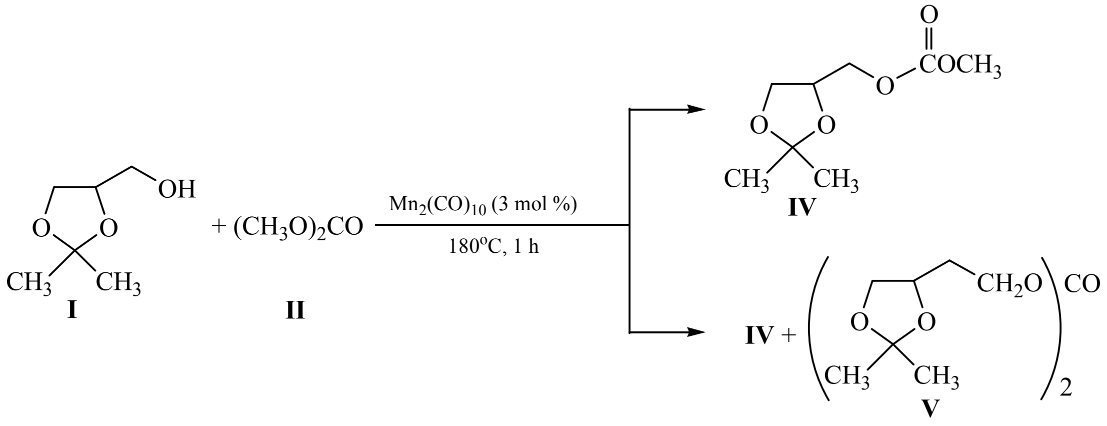
In contrast to $W(CO)_6$, dimanganese decacarbonyl induced conversion of alcohol **I** into non-symmetrical and symmetrical carbonates **IV** and **V**.

When using a (2–8)-fold excess of dimethyl carbonate **II**, diester **V** was formed with selectivity of at least 10%, whereas in a 3-fold molar excess of alcohol **I** the ratio of esters **IV** and **V** in the products mixture was of 2 : 1, but the alcohol conversion did not exceed 10–15% (Scheme 2).

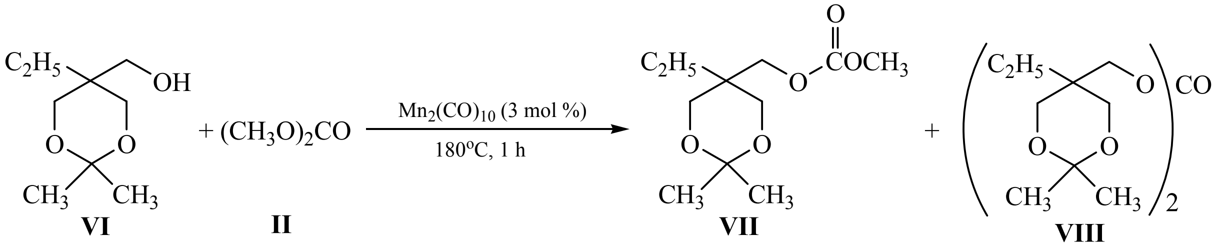
Scheme 1.



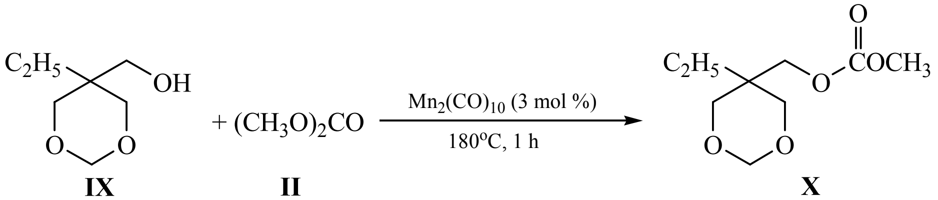
Scheme 2.



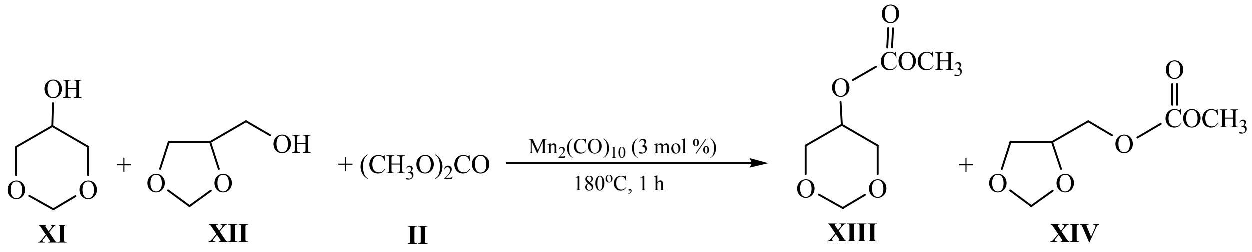
Scheme 3.



Scheme 4.



Scheme 5.

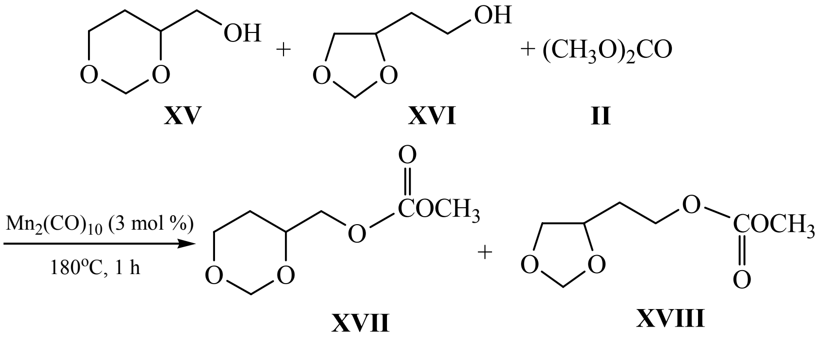


The outcome of etriol isopropylidene derivative **VI** reaction with dimethyl carbonate **II** in the presence of $Mn_2(CO)_{10}$ was similar: when a 4-fold molar excess of carbonate **II** was used, the esters **VII** and **VIII** were formed with overall yield of 90% at a ratio of 24 : 1 (Scheme 3).

The reaction of heterocyclic alcohol **IX** with a 3-fold molar excess of dimethyl carbonate in the presence of $Mn_2(CO)_{10}$ (180°C, 1 h) occurred with high selectivity to give methyl-(5-ethyl-1,3-dioxan-5-yl)methylcarbonate **X** in 84% yield as the only product (Scheme 4).

The reaction of equimolar mixture of alcohols **XI** and **XII** (glycerol formals) with dimethyl carbonate **II** under similar conditions resulted in the formation of equimolar mixture of two carbonates (**XIII** and **XIV**) with overall yield of 56% (Scheme 5).

Scheme 6.



Similarly, the reaction of equimolar mixture of alcohols **XV** and **XVI** (1,2,4-butanetriol formals) with dimethyl carbonate **II** afforded equimolar mixture of non-symmetrical carbonates **XVII** and **XVIII** with overall yield of 88% (Scheme 6).

The results are summarized in the table; in no case the products of the heterocycle degradation were formed.

Additional experiments showed that the used metal carbonyls did not induce decomposition of the model compound, 2,2-dimethyl-1,3-dioxolane, under the reaction conditions.

Note that vanadyl acetylacetonate earlier employed as a transesterification catalyst under the same conditions [5] catalyzed transformation of alcohol **I** into non-symmetrical carbonate **IV** with selectivity of 100%, but the conversion of the alcohol was no more than 15% (180°C, 1 h, **I** : **II** ratio of 1 : 4).

EXPERIMENTAL

^{13}C NMR spectra ($CDCl_3$) were recorded using a Bruker Avance-400 spectrometer (100.62 MHz). Mass spectra were registered with a Shimadzu GCMS-QP2010Plus instrument (capillary column SPB-5, 30 m × 0.25 mm, helium as carrier gas, heating from 40 to 300°C at 8 deg min^{-1}, evaporation temperature 280°C, ion source temperature 200°C, and ionization energy 70 eV). Elemental analysis was performed with a Carlo Erba 1106 analyzer.

The reaction progress was monitored by gas-liquid chromatography using a Shimadzu GC-9A, GC-2014 instrument (column 2 m × 3 mm, stationary phase: 5% Silicone SE-30 supported on Chromaton N-AW-HMDS, heating from 50 to 270°C at 8 deg min^{-1}, 47 mL min^{-1} of helium as carrier gas).

The starting heterocyclic alcohols **I**, **VI**, and **IX**, mixtures of glycerol formals **XI** and **XII**, and of 1,2,4-

Reactions of 1,3-dioxacyclane alcohols with dimethyl carbonate catalyzed by metal carbonyls (catalyst : alcohol = 3 : 100, 180°C)

Alcohol	Catalyst	Time, h	Alcohol-to-carbonate molar ratio	Conversion of alcohol, %	Product (selectivity, %)	
I	$W(CO)_6$	1	1 : 3	50	**III** (100)	–
I	$Mn_2(CO)_{10}$	1	1 : 2	53	**IV** (91)	**V** (9)
I	$Mn_2(CO)_{10}$	6	1 : 4	75	**IV** (95)	**V** (5)
I	$Mn_2(CO)_{10}$	1	1 : 8	90	**IV** (100)	–
I	$Mn_2(CO)_{10}$	1	3 : 1	15	**IV** (67)	**V** (33)
VI	$Mn_2(CO)_{10}$	1	1 : 4	89	**VII** (96)	**VIII** (4)
IX	$Mn_2(CO)_{10}$	1	1 : 3	84	**X** (100)	–
XI	$Mn_2(CO)_{10}$	1	1 : 4	56	**XIII** (100)	–
XII	$Mn_2(CO)_{10}$	1	1 : 4	56	**XIV** (100)	–
XV	$Mn_2(CO)_{10}$	1	1 : 4	88	**XVII** (100)	–
XVI	$Mn_2(CO)_{10}$	1	1 : 4	88	**XVIII** (100)	–

butanetriols **XV** and **XVI** were obtained via condensation of the corresponding triols with carbonyl compounds as described in [6].

Dimethyl carbonate reaction with alcohols *(general procedure).* A stainless steel micro autoclave (17 mL) was charged with 3 mmol of $Mn_2(CO)_{10}$ catalyst, 100 mmol of oxyalkyl-1,3-dioxacycloalkane, and 300–400 mmol of dimethyl carbonate. The reaction mixture was heated at 180°C during 1 h. After the reaction was complete, the reaction mixture was filtered through a layer of Al_2O_3. The unreacted dimethyl carbonate was distilled off, and the residue was distilled under atmospheric or reduced pressure.

4-(Methoxymethyl)-2,2-dimethyl-1,3-dioxolane (III). Yield 50%, bp 73–73.5°C (30 mmHg). ^{13}C NMR spectrum, δ_C, ppm: 26.80 (CH_3), 28.25 (CH_3), 59.24 (OCH_3), 67.86 (C^5), 72.87 (C^6), 77.63 (C^4), 110.93 (C^2). Found, %: C 57.47; H 9.59. $C_7H_{14}O_3$. Calculated, %: C 57.51; H 9.65. *M* 146.184.

Methyl (2,2-dimethyl-1,3-dioxolan-4-yl)methylcarbonate (IV). Yield 90%, bp 97–98°C (10 mmHg). ^{13}C NMR spectrum, δ_C, ppm: 25.28 (CH_3), 26.63 (CH_3), 55.14 (OCH_3), 66.20 (C^5), 67.93 (C^6), 73.25 (C^4), 109.88 (C^2), 155.57 (C=O). Found, %: C 50.47; H 7.39. $C_8H_{14}O_5$. Calculated, %: C 50.52; H 7.42. *M* 190.193.

Methyl (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methylcarbonate (VII). Yield 86%, bp 122–123°C (5 mmHg). ^{13}C NMR spectrum, δ_C, ppm: 6.85 (CH_3), 20.20 (CH_3), 23.73 (C^7), 35.93 (C^5), 54.69 (OCH_3), 64.79 ($C^{4,6}$), 67.50 (C^9), 98.21 (C^2), 155.74 (C=O). Found, %: C 56.79; H 8.63. $C_{11}H_{20}O_5$. Calculated, %: C 56.88; H 8.68. *M* 232.27.

Methyl (5-ethyl-1,3-dioxan-5-yl)methylcarbonate (X). Yield 84%, bp 110–111°C (5 mmHg). ^{13}C NMR spectrum, δ_C, ppm: 6.84 (CH_3), 23.58 (C^7), 36.65 (C^5), 54.75 (OCH_3), 67.26 (C^8), 73.53 ($C^{4,6}$), 94.09 (C^2), 155.67 (C=O). Found, %: C 52.89; H 7.85. $C_9H_{16}O_5$. Calculated, %: C 52.93; H 7.90. *M* 204.22.

Methyl (1,3-dioxan-5-yl)carbonate (XIII). Yield 56%, bp 98–99°C (8 mmHg). ^{13}C NMR spectrum, δ_C, ppm: 54.96 (OCH_3), 69.24 ($C^{4,6}$), 79.89 (C^5), 93.88 (C^2), 155.12 (C=O). Found, %: C 44.39; H 6.18. $C_6H_{10}O_5$. Calculated, %: C 44.45; H 6.22. *M* 162.14.

Methyl (1,3-dioxolan-4-yl)methylcarbonate (XIV). Yield 56%, bp 98–99°C (8 mmHg). ^{13}C NMR spectrum, δ_C, ppm: 54.78 (OCH_3), 69.40 (C^6), 69.53 (C^5), 95.41 (C^2), 155.53 (C=O). Found, %: C 44.39; H 6.18. $C_6H_{10}O_5$. Calculated, %: C 44.45; H 6.22. *M* 162.14.

Methyl (1,3-dioxane-4-yl)methylcarbonate (XVII). Yield 88%, bp 94–95°C (6 mmHg). ^{13}C NMR spectrum, δ_C, ppm: 27.48 (C^5), 54.83 (OCH_3), 65.94 (C^6), 69.42 (C^7), 73.87 (C^4), 93.56 (C^2), 155.61 (C=O). Found, %: C 47.69; H 6.82. $C_7H_{12}O_5$. Calculated, %: C 47.72; H 6.87. *M* 176.167.

Methyl 2-(1,3-dioxolan-4-yl)ethylcarbonate (XVIII). Yield 88%, bp 94–95°C (6 mmHg). ^{13}C NMR spectrum, δ_C, ppm: 32.23 (C^6), 54.83 (OCH_3), 64.76 (C^7), 69.66 (C^5), 77.45 (C^4), 94.85 (C^2), 155.61 (C=O). Found, %: C 47.69; H 6.82. $C_7H_{12}O_5$. Calculated, %: C 47.72; H 6.87. *M* 176.167.

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