

Synthesis of New Substituted 2,3-Dihydro-1,4-dioxin-2-ones and 1,4-Dioxan-2-ones

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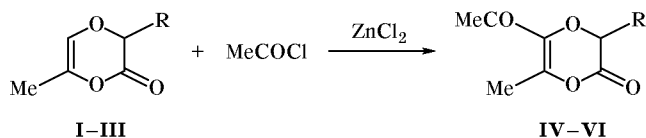
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Abstract—3-Alkyl-6-methyl-2,3-dihydro-1,4-dioxin-2-ones reacted with acetyl chloride in the presence of zinc(II) chloride to give 5-acetyl-3-alkyl-6-methyl-2,3-dihydro-1,4-dioxin-2-ones. Oxidation of the latter with hydrogen peroxide in formic acid, followed by treatment with magnesium bromide, afforded 3-alkyl-6-methyl-1,4-dioxane-2,5-diones. Chlorination of 6-hydroxymethyl-1,4-dioxan-2-ones with thionyl chloride and subsequent dehydrochlorination led to formation of 6-methylene-1,4-dioxan-2-ones.

We previously synthesized 2,5-substituted 2,3-dihydro-1,4-dioxins [1–3]. In continuation of our studies on the synthesis and properties of dihydro-1,4-dioxinones, we have synthesized 3-alkyl-5-acetyl-6-methyl-2,3-dihydro-1,4-dioxin-2-ones by reaction of compounds **I–III** with acetyl chloride in the presence of a catalytic amount of zinc(II) chloride (Scheme 1).

Scheme 1.

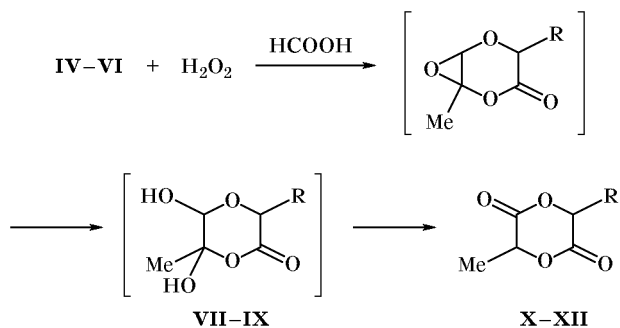


The structure of compounds **IV–VI** was confirmed by IR and ^1H NMR spectroscopy, elemental analysis, and transformations into the corresponding 2,4-dinitrophenylhydrazones (see table). Oxidation of the endocyclic double bond in **IV–VI** with hydrogen peroxide in formic acid (performic acid) leads to 3-alkyl-5,6-dihydroxy-1,4-dioxan-2-ones **VII–IX**. Treatment of the latter with an equimolar amount of magnesium bromide affords 3-alkyl-6-methyl-1,4-dioxane-2,5-diones **X–XII** (Scheme 2).

Dioxanediones **X–XII** are crystalline substances; their structure was confirmed by the IR and ^1H NMR spectra (see table). The IR spectra of products **X–XII** lack absorption of double C=C bond, but strong bands are observed in the regions 1110–1108 and 1785–1780 cm^{-1} .

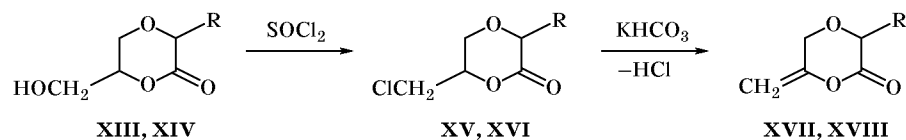
By reaction of 3-alkyl-6-hydroxymethyl-1,4-dioxan-2-ones **XIII** and **XIV** [4] with thionyl chloride we obtained 3-alkyl-6-chloromethyl-1,4-dioxan-2-ones **XV** and **XVI** (Scheme 3). Treatment of chloromethyl derivatives **XV** and **XVI** with potassium hydrogen carbonate gave 3-alkyl-6-methylene-1,4-dioxan-2-ones **XVII** and **XVIII**. The use of alkali metal alkoxides leads to opening of the dioxane ring.

Scheme 2.



The structure of compounds **XVII** and **XVIII** was confirmed by IR and ^1H NMR spectroscopy. The presence of a double bond was detected by chemical reactions (with bromine and potassium permanganate). The structure of these products was also proved by successive hydrochlorination and dehydrochlorination of **XVIII**, which afforded 3,6-dimethyl-2,3-dihydro-1,4-dioxan-2-one (**II**) [2].

Scheme 3.



XIII, XV, XVII, R = H; XIV, XVI, XVIII, R = Me.

It is known [4] that 1,4-dioxan-2-one selectively absorbs carbon(II) oxide from exhaust gas. We have found that 3,6-substituted 1,4-dioxan-2-ones also selectively absorb carbon(II) oxide from combustion products of gasoline and diesel fuel [5]. Ecological properties of newly synthesized compounds **IV–VI**, **IX–XII**, **XVII**, and **XVIII** are now under study.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument (Carl Zeiss), and the ^1H NMR spectra were obtained on a Varian-300 spectrometer using TMS as internal reference. The purity of the initial compounds was checked, and the product composition was determined, by GLC on an LKhM-72M chromatograph

using a steel column, 2000×4 mm, packed with 5% of SE-30 on Chromosorb PAW; carrier gas helium, flow rate 60 ml/min; thermal conductivity detector; oven temperature 453–473 K. Thin-layer chromatography was performed on Silufol UV-254 plates (1-butanol–acetic acid–50% aqueous acetone, 40:40:20; development with iodine vapor).

3-Alkyl-5-acetyl-6-methyl-2,3-dihydro-1,4-dioxin-2-ones IV–VI were synthesized following the procedure described in [6]. Their yields, melting points, and analytical and spectral data are given in table.

3-Alkyl-6-methyl-1,4-dioxane-2,5-diones X–XII. 3-Alkyl-5-acetyl-6-methyl-2,3-dihydro-1,4-dioxin-2-ones **IV–VI** were oxidized as described in [6]. The

Yields, melting points, elemental analyses, and spectral parameters of 2,3-dihydro-1,4-dioxan-2-ones **IV–VI** and 1,4-dioxane-2,5-diones **X–XII**

Comp. no.	Yield, %	mp, °C	Found, %		Calculated, %		IR spectrum, ν , cm^{-1}	^1H NMR spectrum, δ , ppm	R_f
			C	H	C	H			
IV^a	61.3	59–61	53.87	5.21	53.85	5.13	1730 (C=O) 1660 (C=C) 1108 (COC)	5.6 d (3), $J = 7.2$ Hz 7.7 s (7), $J = 11.8$ Hz 8.2 s (8), $J = 10.7$ Hz	0.41
V^b	58.0	56	56.53	5.93	56.47	5.88	1745 (C=O) 1665 (C=C) 1110 (COC)	4.4 q (3), $J = 7.4$ Hz 7.6 s (7), $J = 13.0$ Hz 8.1 s (8), $J = 12.7$ Hz	0.42
VI^c	63.1	72–73	58.74	6.60	58.69	6.52	1745 (C=O) 1660 (C=C) 1112 (COC)	4.5 m (3), $J = 7.3$ Hz 7.7 s (7), $J = 12.3$ Hz 8.0 s (8), $J = 13.3$ Hz	0.40
X	63.7	70–71	46.27	4.63	46.15	4.61	1780 (C=O) 1108 (COC)	4.7 d (3), $J = 7.5$ Hz 8.6 q (6), $J = 10.1$ Hz 8.8 d (7), $J = 8.4$ Hz	0.41
XI	65.0	89–90	49.88	5.53	50.00	5.55	1785 (C=O) 1112 (COC)	4.8 q (3), $J = 7.6$ Hz 8.6 q (6), $J = 9.8$ Hz 8.7 d (7), $J = 8.3$ Hz	0.41
XII	62.5	74–76	53.10	6.29	53.16	6.33	1780 (C=O) 1110 (COC)	–	0.44

^a 2,4-Dinitrophenylhydrazine: mp 106–108°C; found, %: N 16.82; calculated, %: N 16.66.

^b 2,4-Dinitrophenylhydrazine: mp 118–119°C; found, %: N 16.11; calculated, %: N 16.00.

^c 2,4-Dinitrophenylhydrazine: mp 133–144°C; found, %: N 15.45; calculated, %: N 15.38.

6-Chloromethyl-1,4-dioxan-2-one (XV). Compound **XIII** was treated with thionyl chloride according to the procedure described in [7]. Yield 12.34 g (82%), mp 54–55°C (from chloroform–petroleum ether, 1:1). IR spectrum, ν , cm^{-1} : 1113–1107 (COC); 1782 (C=O); 842 (C–Cl). ^1H NMR spectrum, δ , ppm: 4.3 d (CH_2Cl ; $^2J = 7.2$ Hz). Found, %: C 39.89; H 4.63; Cl 23.59. $\text{C}_5\text{H}_7\text{ClO}_3$. Calculated, %: C 39.87; H 4.65; Cl 23.62.

6-Chloromethyl-3-methyl-1,4-dioxan-2-one (XVI). 6-Hydroxymethyl-3-methyl-1,4-dioxan-2-one (**XIV**) was treated with thionyl chloride in pyridine as described in [6]. Yield 9.91 g (87%); bp 89–91°C (2 mm); $n_{\text{D}}^{20} = 1.5099$; $d_4^{20} = 1.3785$. $MR_{\text{D}} = 35.71$; calculated: 35.87. IR spectrum, ν , cm^{-1} : 1111–1108 (COC); 1780 (C=O); 835 (C–Cl). ^1H NMR spectrum, δ , ppm: 4.5 d (CH_2Cl ; $^2J = 7.3$ Hz). Found, %: C 43.75; H 5.45; Cl 21.52. $\text{C}_6\text{H}_9\text{ClO}_3$. Calculated, %: C 43.77; H 5.47; Cl 21.58.

6-Methylene-1,4-dioxan-2-one (XVII). A solution of 0.066 mol of potassium hydrogen carbonate in 20 ml of water and 10 ml of dimethylformamide was added to 0.03 mol of 6-halomethyl-1,4-dioxan-2-one. The mixture was heated for 20–22 h under reflux with stirring. It was then cooled, and the precipitated salt was filtered off and washed with petroleum ether on a filter. The filtrate was combined with the washings, petroleum ether was distilled off, and the residue was distilled in a vacuum. Yield 7.0 g (62%); bp 90–92°C (4 mm); $n_{\text{D}}^{20} = 1.4210$; $d_4^{20} = 1.1120$. $MR_{\text{D}} = 25.99$. IR spectrum, ν , cm^{-1} : 1652 m (C=C); 1112–1108 (COC); 1780 (C=O). ^1H NMR spectrum, δ , ppm: 4.6 s ($=\text{CH}_2$; $^2J = 2.7$ Hz). Found, %:

C 52.64; H 5.26. $\text{C}_5\text{H}_6\text{O}_3$. Calculated, %: C 52.63; H 5.26.

3-Methyl-6-methylene-1,4-dioxan-2-one (XVIII) was synthesized in a similar way. Yield 8.3 g (65%); bp 103–105°C (4 mm); $n_{\text{D}}^{20} = 1.4236$; $d_4^{20} = 1.0686$; $MR_{\text{D}} = 30.54$. IR spectrum, ν , cm^{-1} : 1655 (C=C); 1780 (C=O). ^1H NMR spectrum, δ , ppm: 4.5 s ($=\text{CH}_2$; $^2J = 2.8$ Hz). Found, %: C 52.27; H 6.27; $\text{C}_6\text{H}_8\text{O}_3$. Calculated, %: C 56.25; H 6.25.

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