

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

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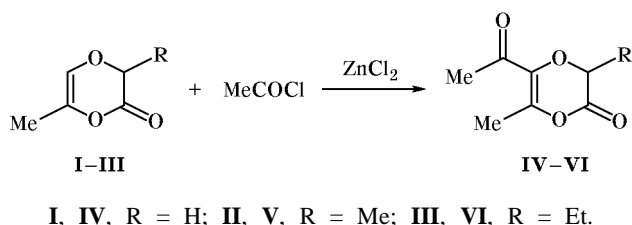
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Abstract—3-Alkyl-6-methyl-2,3-dihydro-1,4-dioxin-2-ones reacted with acetyl chloride in the presence of zinc(II) chloride to give the corresponding 3-alkyl-5-acetyl-6-methyl-2,3-dihydro-1,4-dioxin-2-ones. Oxidation of the latter with hydrogen peroxide in formic acid, followed by treatment with magnesium bromide, afforded 3-alkyl-6-methyl-1,4-dioxane-2,5-diones. Successive chlorination and dechlorination of 6-hydroxymethyl-1,4-dioxan-2-ones yielded 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 preparation 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 3-alkyl-6-methyl-2,3-dihydro-1,4-dioxin-2-ones **I–III** with acetyl chloride in the presence of a catalytic amount of zinc(II) chloride (Scheme 1).

Scheme 1.



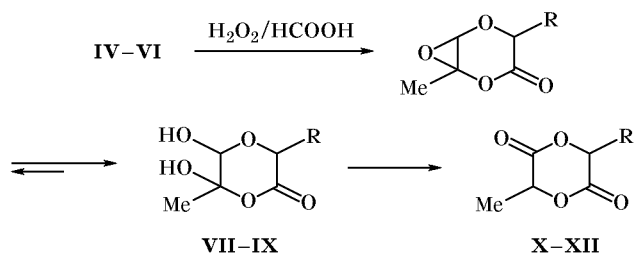
The structure of products **IV–VI** was confirmed by the IR and ^1H NMR spectra, elemental analyses, and their conversion into the corresponding 2,4-dinitro-

phenylhydrazones (see table). Oxidation of the endocyclic double bond in **IV–VI** with hydrogen peroxide in formic acid (performic acid) gave 3-alkyl-5,6-dihydroxy-1,4-dioxan-2-ones **VII–IX**. The latter were treated with an equimolar amount of magnesium bromide to obtain 3-alkyl-6-methyl-1,4-dioxane-2,5-diones **X–XII** (Scheme 2).

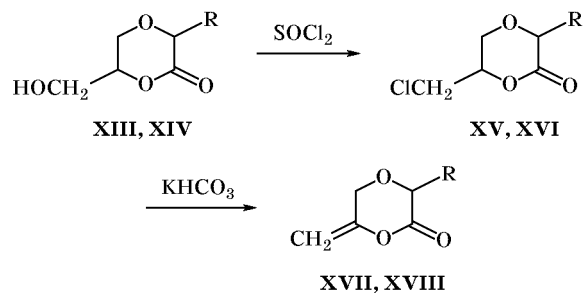
Dioxanediones **X–XII** are crystalline substances. Their structure was proved by the IR and ^1H NMR spectra (see table). The IR spectra of **X–XII** lack characteristic absorption due to stretching vibrations of the double bond but contain strong bands at 1110–1108 and 1785–1780 cm^{-1} , respectively.

The reaction of 3-alkyl-6-hydroxymethyl-1,4-dioxan-2-ones **XIII** and **XIV** [4] with thionyl chloride in pyridine afforded 3-alkyl-6-chloromethyl-1,4-dioxan-2-ones **XV** and **XVI**. Treatment of the latter with potassium hydrogen carbonate resulted in formation of 6-methylene derivatives **XVII** and **XVIII** (Scheme 3). The use of alkali metal alkoxides as

Scheme 2.



Scheme 3.



2-Dihydro-1,4-dioxin-2-ones **IV–VI** and 1,4-dioxane-2,5-diones **X–XII**

Comp. no.	Yield, %	mp, °C	R_f	Found, %		Formula	Calculated, %		IR spectrum, ν , cm^{-1}	^1H NMR spectrum, δ , ppm (J , Hz)
				C	H		C	H		
IV	61.3	59–61	0.41	53.87	5.21	$\text{C}_7\text{H}_8\text{O}_4$	53.85	5.13	1730 (C=O) 1660 (C=C) 1108 (COC)	5.6 d (3), $J = 7.2$ 7.7 s (7), $J = 11.8$ 8.2 s (8), $J = 10.7$
V	58.0	56	0.42	56.53	5.93	$\text{C}_8\text{H}_{10}\text{O}_4$	56.47	5.88	1745 (C=O) 1665 (C=C) 1110 (COC)	4.4 q (3), $J = 7.4$ 7.6 s (7), $J = 13.0$ 8.1 s (8), $J = 12.7$
VI	63.1	72–73	0.40	58.74	6.60	$\text{C}_9\text{H}_{12}\text{O}_4$	58.69	6.52	1745 (C=O) 1660 (C=C) 1112 (COC)	4.5 m (3), $J = 7.3$ 7.7 s (7), $J = 12.3$ 8.0 s (8), $J = 13.3$
X	63.7	70–71	0.41	46.27	4.63	$\text{C}_5\text{H}_6\text{O}_4$	46.15	4.61	1780 (C=O) 1108 (COC)	4.7 d (3), $J = 7.5$ 8.6 q (6), $J = 10.1$ 8.8 d (7), $J = 8.4$
XI	65.0	89–90	0.41	49.88	5.53	$\text{C}_6\text{H}_8\text{O}_4$	50.00	5.55	1785 (C=O) 1112 (COC)	4.8 q (3), $J = 7.6$ 8.6 q (6), $J = 9.8$ 8.7 d (7), $J = 8.3$
XII	62.5	74–76	0.44	53.10	6.29	$\text{C}_8\text{H}_{10}\text{O}_4$	53.16	6.33	1780 (C=O) 1110 (COC)	–

dehydrohalogenating agents leads to opening of the dioxane ring.

The structure of compounds **XVII** and **XVIII** was confirmed by the IR and ^1H NMR spectra. The presence of a double bond therein was proved by chemical tests (reactions with bromine and potassium permanganate). Successive hydrochlorination and dehydrochlorination of **XVIII** afforded 3,6-dimethyl-2,3-dihydro-1,4-dioxin-2-one which was described by us previously [2].

1,4-Dioxan-2-one is known to selectively absorb carbon(II) oxide from exhaust gas [4]. We have found that 3,6-substituted 1,4-dioxan-2-ones also selectively absorb carbon(II) oxide from products of combustion of carburant and diesel fuel [5]. Examination of the ecological parameters of eight newly synthesized compounds **IV–VI**, **IX–XII**, **XVII**, and **XVIII** is now in progress.

EXPERIMENTAL

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

chromatograph equipped with a steel column, 2000 \times 4 mm, which was packed with 5% of SE-30 on Chromosorb PAW; carrier gas helium, flow rate 60 ml/min; heat conductivity detector; oven temperature 453–473 K; as well as by TLC on Silufol UV-254 plates (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 by the procedure described in [6]. Their properties are given in table. 2,4-Dinitrophenyl hydrazones: **IV**, mp 106–108°C. Found, %: N 16.82. $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_6$. Calculated, %: N 16.66; **V**, mp 118–119°C. Found, %: 16.11. $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_6$. Calculated, %: N 16.00; **VI**, mp 133–144°C. Found, %: N 15.45. $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_6$. Calculated, %: N 15.38.

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 by the procedure described in [6]. The resulting 3-alkyl-5,6-dihydroxy-6-methyl-1,4-dioxan-2-ones (without isolation) were heated for 3–5 h in boiling toluene containing an equimolar amount of magnesium bromide. The mixture was cooled to room temperature and washed with cold water. The organic layer was separated, washed over anhydrous magnesium sulfate, and evaporated, and the

residue was recrystallized from acetone–ethyl acetate 1:1 (see table).

6-Chloromethyl-1,4-dioxan-2-one (XV). Compound **XIII** was chlorinated 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, following the procedure described in [7]. 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 compound **XVI**, and the mixture was heated for 20–22 h under reflux with stirring. The mixture was cooled and filtered, and the precipitate was washed on a filter with petroleum ether. The filtrate was combined with the washings, petroleum ether was distilled off, and the residue was distilled under reduced pressure. 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=CH₂), 1112–1108 (COC), 1780 (C=O). ^1H NMR spectrum, δ , ppm: 4.6 s (C=CH₂, $^2J = 2.7$ 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 as described above for compound **XVII**. 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=CH₂), 1780 (C=O). ^1H NMR spectrum, δ , ppm: 4.5 s (C=CH₂, $^2J = 2.8$ 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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