

Oxidation of 1,3-Dioxacycloalkanes with Complexes of Potassium Chlorochromate and Chlorodiperoxochromate with 15-Crown-5, Catalyzed with 2,2,5,5-Tetramethyl-4-phenyl-3-oxo-3 λ^5 -imidazolin-1-yloxyl

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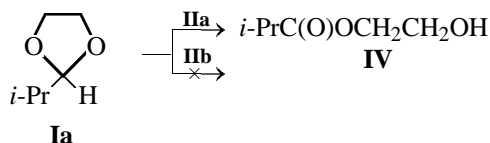
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Abstract—2,2,5,5-Tetramethyl-4-phenyl-3-oxo-3 λ^5 -imidazolin-1-yloxyl catalyzes oxidation of 2-isopropyl-1,3-dioxolane, 2-phenyl-1,3-dioxolane, 2-phenyl-4-chloromethyl-1,3-dioxolane, and 2-phenyl-1,3-dioxane with 15-crown-5 complexes of potassium chlorodiperoxochromate ($\text{KCrO}_5\text{Cl} \cdot 2\text{C}_{10}\text{H}_{20}\text{O}_5$) and potassium chlorochromate ($\text{KCrO}_3\text{Cl} \cdot 2\text{C}_{10}\text{H}_{20}\text{O}_5$). 2-Isopropyl-1,3-dioxolane is oxidized to the corresponding monoester in quantitative yield, and the 2-phenyl derivatives yield benzaldehyde. The spiro ketal, 2,2-pentamethylene-4-methyl-1,3-dioxane, is decomposed to cyclohexanone.

Oxidation of cyclic acetals with oxygen, ozone, hydroperoxides, and other agents yields, as a rule, the corresponding glycol monoesters [1–4]. It was interesting to study oxidation of 1,3-dioxacycloalkanes with new oxidants: complexes of potassium chlorochromate and chlorodiperoxochromate with 15-crown-5 [5, 6].

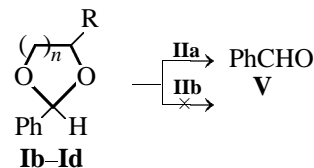
We have studied oxidation of cyclic acetals: 2-isopropyl-1,3-dioxolane **Ia**, 2-phenyl-1,3-dioxolane **Ib**, 2-phenyl-4-chloromethyl-1,3-dioxolane **Ic**, 2-phenyl-1,3-dioxane **Id**, and 2,2-pentamethylene-4-methyl-1,3-dioxane **Ie** with 2 : 1 15-crown-5 complexes of potassium chlorodiperoxochromate (**IIa**) and potassium chlorochromate (**IIb**) in the absence and in the presence of 2,2,5,5-tetramethyl-4-phenyl-3-oxo-3 λ^5 -imidazolin-1-yloxyl **III**.

We found that acetal **Ia** is slowly oxidized with complex **IIa** to ethylene glycol monoisobutyrate **IV**. The yield of **IV** in 7 h at 60°C does not exceed 10%.



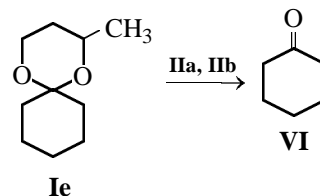
Complex **IIb** does not react with **Ia** under these conditions.

2-Phenyl-1,3-dioxacycloalkanes **Ib–Id** vigorously react with **IIa**, with breakdown of the acetal moiety and regeneration of benzaldehyde **V** in 50–70% yield. Complex **IIb** does not react with **Ib–Id** under these conditions.



I, $n = 1$, $\text{R} = \text{H}$ (**b**); $n = 1$, $\text{R} = \text{CH}_2\text{Cl}$ (**c**); $n = 2$, $\text{R} = \text{H}$ (**d**).

The spiro ketal, 2,2-pentamethylene-4-methyl-1,3-dioxane **Ie**, under the action of **IIa** or **IIb** decomposes almost quantitatively to the initial ketone, cyclohexanone **VI**.



In the presence of catalytic amounts of stable radi-

[†] Deceased.

Oxidation of cyclic acetals DH with complexes of 15-crown-5 with potassium chlorodiperoxochromate (**IIa**) and chlorochromate (**IIb**) (CH₃CN, 60°C, [DH]/[**III**] 1 : 0.01)

DH	Oxidant	[DH]/ oxidant	Reaction product	Yield, %
Ia	IIa	1 : 3	IV	10
	IIa + III	1 : 3	IV	~100
	IIb	1 : 6	—	—
	IIb + III	1 : 6	IV	~100
Ib	IIa	1 : 3	V	70
	IIa + III	1 : 3	V	~100
	IIb	1 : 3	—	—
	IIb + III	1 : 3	V	~100
Ic	IIa	1 : 3	—	—
	IIa + III	1 : 3	V	~100
	IIb	1 : 6	—	—
	IIb + III	1 : 6	V	~100
Id	IIa	1 : 3	V	50
	IIa + III	1 : 3	V	~100
	IIb	1 : 6	—	—
	IIb + III	1 : 6	V	~100
Ie	IIa	1 : 3	VI	~100
	IIb	1 : 6	VI	95

cal **III**, which is known [7] to promote liquid-phase oxidation, compound **Ia** is converted almost quantitatively into **IV** under the action of both complex **IIa** and complex **IIb**. Catalytic oxidation of **Ib–Ie** gives aldehyde **V** in ≥90% yield (see table).

The higher activity of **IIa** is probably due to the presence of weak O–O bonds [6]. In reaction with **IIa**, six-membered acetal **Id** is less active than its five-membered analog **Ib**.

To conclude, agents **IIa** and **IIb** can be successfully used for removing the acetal protective group from aromatic aldehydes and from ketones.

EXPERIMENTAL

The oxidation products were identified and analyzed with a Finnigan gas chromatograph–mass spectrometer, by GLC (Chrom-5, 1200 × 3-mm column, SE-30 stationary phase), and by ¹H and ¹³C NMR spectroscopy (Bruker AM-300 spectrometer, 300 and 75 MHz, respectively; CDCl₃, reference TMS). As references we used specially prepared monoester **IV** and reagent-grade carbonyl compounds **V** and **VI**.

The initial cyclic acetals **Ia–Ie** were prepared as described in [8]. Complexes **IIa** and **IIb** were prepared according to [5, 6]. Nitroxyl radical **III** was purified by recrystallization from hexane.

Oxidation was performed in a 30-ml temperature-controlled glass vessel, stirred with a magnetic stirrer. To a solution of 1 mmol of acetal in 10 ml of acetonitrile we added 3 g of moist alumina and heated to 60°C. Then 3–6 mmol of **IIa** or **IIb** was added in portions over a period of 1 h, and stirring was continued for an additional 6–7 h. The resulting mixture was cooled to room temperature and filtered. The solvent was removed on a rotary evaporator, and the products were analyzed.

Oxidation in the presence of 2,2,5,5-tetramethyl-4-phenyl-3-oxo-3λ⁵-imidazolin-1-yloxy was performed similarly. A solution of 1 mmol of acetal, 1 mmol of KBr, and 0.01 mmol of **III** in 10 ml of acetonitrile was heated to 60°C, 3–6 mmol of **IIa** or **IIb** was added in portions over a period of 1 h, and stirring was continued for an additional 6–7 h. The resulting mixture was cooled to room temperature and filtered; the solvent was evaporated.

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