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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Transformations of Cyclic Acetals under the Action of Some Organic and Inorganic Oxidants

Z. F. Akbalina, S. S. Zlotskii, N. N. Kabal'nova, I. A. Grigor'ev, S. A. Kotlyar, and V. V. Shereshovets

Ufa State Petroleum Engineering University, Ufa, Bashkortostan, Russia
Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, Bashkortostan, Russia

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Abstract—Liquid-phase oxidation of cyclic acetals and 2,2-disubstituted 1,3-dioxacyclanes with dimethyldioxirane, Caro salt, potassium persulfate, and complex of potassium chlorodiperoxochromate with 15-crown-5 was studied.

Liquid-phase oxidation of cyclic acetals receives much attention as a route to hydroperoxides, peroxides, glycol monoesters, and other valuable organic compounds [1]. Such oxidants as oxygen, ozone, organic hydroperoxides, and nitrogen(II) and (IV) oxides were used [2]; however, search for agents ensuring high selectivity of acetal oxidation remains an urgent problem.

In this work, we studied transformations of cyclic acetals and 2,2-disubstituted 1,3-dioxacyclanes under the action of dimethyldioxirane, Caro salt $K_2SO_4 \cdot 2KHSO_5 \cdot KHSO_4$, potassium persulfate, and complex of potassium chlorodiperoxochromate with 15-crown-5.

EXPERIMENTAL

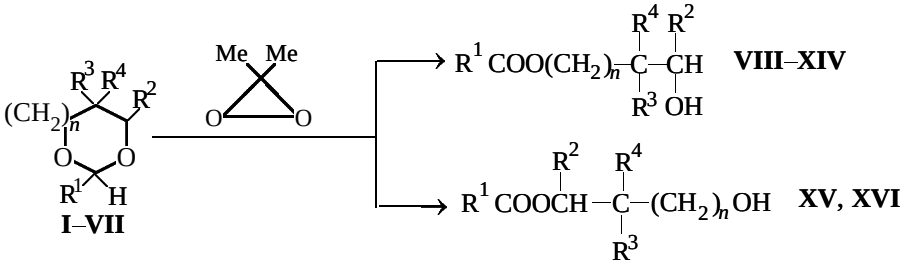
The initial 1,3-dioxacycloalkanes **I**–**VII** [3, 4], dimethyldioxirane [5], Caro salt [6], and complex of potassium chlorodiperoxochromate with 15-crown-5 [7] were prepared by published procedures. Stable nitroxyl radical, 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-3-oxide-1-oxyl, was prepared according to [8]. Oxidation with dimethyldioxiane was performed as described in [9].

Oxidation with Caro salt was performed in a 30-ml temperature-controlled glass vessel stirred with a magnetic stirrer. To a solution of 1 mmol of a substrate in 10 ml of chloroform, 3 g of wet alumina was added, and the mixture was heated to 50°C. Caro salt (3 mmol) was added in portions over a period of 1 h, and stirring was continued for 2–5 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 nitroxyl radical was performed similarly.

Oxidation with potassium persulfate and complex of potassium chlorodiperoxochromate with 15-crown-5 was performed in acetonitrile at 60°C for 7 h, molar ratio substrate : oxidant 1 : 3.

The reaction products were identified and analyzed by ^1H and ^{13}C NMR spectroscopy (Bruker 300 spectrometer, 300 and 75 MHz, respectively; reference TMS, solvent $CDCl_3$), GC–MS (Finnigan), and GLC (Chrom-5, 1200 × 3-mm column, stationary phase SE-30), using authentic samples of the monoesters and ketones.

We found that cyclic acetals **I**–**VII** react with dimethyldioxirane with quantitative formation of the corresponding glycol monoesters **VIII**–**XVI**:



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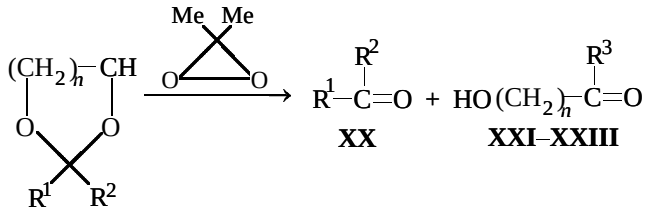
where n = 0, R^1 = *i*-Pr (**I**, **VIII**), Ph (**II**, **IX**), R^2 = R^3 = R^4 = H (**I**, **II**, **VIII**, **IX**); n = 1, R^1 = *i*-Pr (**III**, **X**), Ph (**IV**, **XI**), R^2 = R^3 = R^4 = H (**III**, **IV**, **X**, **XI**); R^1 = *i*-Pr (**V**, **XII**, **XV**), Ph (**VI**, **XIII**, **XVI**), R^2 = Me, R^3 = R^4 = H (**V**, **VI**, **XII**, **XIII**, **XV**, **XVI**); R^1 = Ph (**VIII**, **XIV**), R^2 = H, R^3 = R^4 = Me (**VII**, **XIV**).

From **V** and **VI**, both isomeric esters **XII** and **XV**, **XIII** and **XVI** are formed, since the C^2–O^1 and C^2–O^3 bonds are cleaved concurrently. According to the ^{1}H and ^{13}C NMR data, under conditions of our experiments, esters **XII** and **XIII** with the secondary hydroxy group are the major products.

2,2-Disubstituted 1,3-dioxacyclanes **XVII**–**XIX** under the action of dimethyldioxirane decompose to the corresponding ketones **XX**:



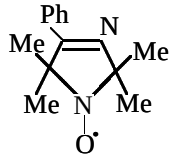
XVII–**XIX** **XX** **XXI**–**XXIII**

where n = 1, R^1 = R^2 = Me, R^3 = H (**XVII**, **XX**, **XXI**); R^1 = R^2 = Me, R^3 = CH_2OH (**XVIII**); n = 2, R^1 = R^2 = R^3 = Me (**XIX**, **XXII**, **XXIII**).

Apparently, in the first stage compounds **XVII**–**XIX** give the corresponding unstable 4-hydroxy-1,3-dioxacyclanes, subsequently decomposing to give ketones **XX**.

It is known [5] that dimethyldioxirane is prepared using Caro salt. We found that this agent oxidizes 2-alkyl-1,3-dioxacyclanes **I** and **III** in the presence of alumina to the corresponding monoesters **VIII** and **X**. However, benzaldehyde derivatives **II** and **VI** under these conditions, along with monoesters **IX** and **XI**, give also benzaldehyde (Table 1).

We found that oxidation of cyclic acetals with Caro salt in the presence of stable nitroxyl radical 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-3-oxide-1-oxyl **XXIV**



XXIV

allows preparation of monoesters **VIII**–**XI** in quantitative yield (Table 1). The catalytic effect of nitroxyl radicals was noted previously in [10].

Table 1. Oxidation of acetals **I**–**IV** with Caro salt in the presence of alumina (A) or radical **XXIV** (B). Solvent $CHCl_3$, 50°C, 2 h

Acetal	Monoester	Yield of monoester, A (B), %
I	**VIII**	40 (99)
II	**IX**	76* (97)
III	**X**	38 (94)
IV	**XI**	45** (96)

* 13% benzaldehyde. ** 25% benzaldehyde.

Table 2. Oxidation of dioxacycloalkanes **I**–**IV** with the complex $KCrO_5Cl \cdot 2C_{10}H_{20}O_5$ in the absence (A) and in the presence (B) of the radical. Solvent MeCN, 60°C, 2 h; molar ratio substrate : oxidant 1 : 3, substrate : radical 1 : 0.01

Substrate	Product	Product yield, A (B), %
I	**VIII**	55 (≥99)
II	PhCHO	88 (≥99)
III	**X**	≤1 (≥99)
IV	PhCHO	65 (≥99)

In the series of 1,3-dioxacycloalkanes **I**–**VI**, only compounds **I** and **II** are oxidized with potassium persulfate $K_2S_2O_8$ to form, in the first case, ethylene glycol monoisobutyrate **VIII** (yield 45%) and, in the second case, benzaldehyde (yield 25%). In the presence of catalytic amounts of **XXIV**, compounds **I**–**VI** afford esters **VIII**–**XIII** in quantitative yield.

We also studied oxidation of cyclic acetals **I**–**IV** with the complex of potassium chlorodiperoxochromate $KCrO_5Cl$ with 15-crown-5 $C_{10}H_{20}O_5$. We found that acetals **I** and **III** are oxidized with this complex to the corresponding monoesters **VIII** and **X**. At the same time, 2-phenyl derivatives **II** and **IV** are selectively oxidized to benzaldehyde (Table 2). Catalytic amounts of nitroxyl radical **XXIV** provide complete conversions of acetals even in 2 h (Table 2).

Thus, complex of potassium chlorodiperoxochromate with 15-crown-5 can be successfully used for removing acetal protective groups from aromatic aldehydes.

CONCLUSION

Dimethyldioxirane, Caro salt, and complex of potassium chlorodiperoxochromate with 15-crown-5 efficiently oxidize polycyclic acetals to the corre-

sponding glycol moonoesters. 2,2-Disubstituted 1,3-dioxacyclanes under these conditions decompose to the corresponding ketones. Additions of catalytic amounts of the nitroxyl radical increase the reaction yield.

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