

Oxidative transformation of 1,3-dioxacycloalkanes induced by chlorine dioxide

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The products and kinetic regularities of the reactions of 1,3-dioxacycloalkanes with chlorine dioxide were studied. The effects of the nature of solvent and the temperature on the reaction rate were considered and the activation parameters were determined.

Key words: chlorine dioxide, 1,3-dioxacycloalkanes, kinetics, products.

The products of oxidative transformations of 1,3-dioxacycloalkanes and their derivatives find extensive practical application.^{1,2} Chlorine dioxide is of obvious interest as an oxidant. Meanwhile, data on reactions of chlorine dioxide in nonaqueous media are virtually missing.

In this work, we studied the products and the kinetic regularities of the reaction of chlorine dioxide with 1,3-dioxacycloalkanes (DH) of various structures: 2-isopropyl-1,3-dioxolane (**1**), 2-phenyl-1,3-dioxolane (**2**), 2,2-pentamethylene-1,3-dioxolane (**3**), 4-chloromethyl-1,3-dioxolane (**4**), 4-chloromethyl-2-phenyl-1,3-dioxolane (**5**), 4-methyl-1,3-dioxane (**6**), 2-isopropyl-4-methyl-1,3-dioxane (**7**), 4-methyl-2-phenyl-1,3-dioxane (**8**), and 5,5-dimethyl-2-phenyl-1,3-dioxane (**9**).

Experimental

Chlorine dioxide was prepared by the reaction of potassium chlorate with oxalic acid in the presence of sulfuric acid according to a known procedure.³ The concentration of ClO₂ was determined by spectrophotometry on a Specord M40 instrument at λ_{max} = 360 nm. Solvents were purified by standard procedures.⁴

The starting 1,3-dioxacycloalkanes and the reaction products were analyzed by GLC using a Chrom 5 chromatograph (3.5 m × 3 mm column, 5% SE-30 on Chromaton) and by ¹H and ¹³C NMR spectroscopy on a Bruker AM-300 instrument (300 MHz). The solvents used were CDCl₃ (99.8 at.% D; Aldrich) and acetone-d₆ (99.9 at.% D; Aldrich).

Oxidation of 1,3-dioxacycloalkanes with chlorine dioxide (general procedure). 1,3-Dioxacycloalkane (0.86–4.0 mmol) in 3 mL of MeCN was maintained at 35 °C and a specified amount of

ClO₂ (1.24–6.0 mmol) in a known concentration was added. The reaction was carried out for 4–7 h. The solvent was evaporated and the reaction products were identified.

Oxidation of 1,3-dioxanes with chlorine dioxide in the presence of 2,2,5,5-tetramethyl-4-phenyl-3-imidazolin-1-oxyl 3-oxide (general procedure). A specified amount of 1,3-dioxane (0.86–4.0 mmol) in MeCN (3 mL) was placed in a reactor, the iminoxyl radical (>N–O[•]) and KBr were added, and then the specified amount of a solution of ClO₂ with a known concentration was introduced. The reaction was carried out for 4 h at 35 °C. Acetonitrile was evaporated and the reaction products were identified. The ratio [DH] : [>N–O[•]] : [KBr] : [ClO₂] = 1 : 0.01 : 1 : 2.

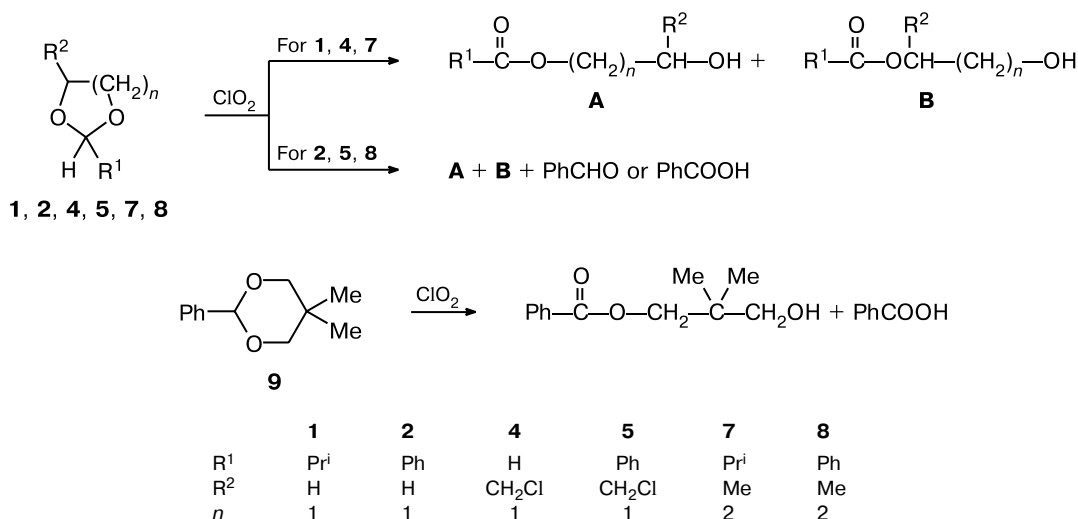
The kinetics of oxidation of 1,3-dioxacycloalkanes with chlorine dioxide was studied by monitoring the consumption of ClO₂. The change in chlorine dioxide concentration was determined by spectrophotometry (Specord M40, Carl Zeiss Jena) by monitoring the decrease in the optical density at λ_{max} in thermostated quartz cells (the optical lengths were 1 and 0.1 cm, the error was ≤5%). The concentration of 1,3-dioxacycloalkanes and ClO₂ was varied in the ranges of 0.04–3.2 and (4–8) · 10^{–3} mol L^{–1}, respectively. Benzene, acetone, MeCN, CCl₄, AcOEt, EtOH, and MeOH were used as solvents. The temperature was varied in the range of 30.6–61 °C.

Results and Discussion

Reaction products. The oxidation of compounds **1**, **2**, and **4–9** with chlorine dioxide gives the corresponding glycol monoesters, their yield reaching 60% (Scheme 1, Tables 1, 2). The oxidation of nonsymmetrical 1,3-dioxacycloalkanes **4**, **5**, **7**, and **8** affords a mixture of two isomeric esters of types **A** and **B** in 2 : 1 ratio. The reaction of 1,3-dioxolane **3** with ClO₂ results in cyclohexanone (82%) and the product of its chlorination, chlorocyclo-

[†] Deceased.

Scheme 1



hexanone. The reaction of ClO₂ with cyclic acetals containing a Ph substituent in position 2 gives, in addition to monoesters, benzaldehyde and/or benzoic acid (see Scheme 1).

The use of iminoxyl radicals in the oxidation is due to the fact that they are able to form oxoammonium salts, which are potent oxidizing agents.⁵ Oxygen, hydrogen peroxide, and sodium hypochlorite are used most often as primary oxidants.^{5,6} Therefore, the increase in the product yield in the oxidation of 1,3-dioxacycloalkanes with

chlorine dioxide in the presence of 2,2,5,5-tetramethyl-4-phenyl-3-imidazolin-1-oxyl 3-oxide can be explained by the action of the oxoammonium salt resulting from the reaction of the iminoxyl radical with chlorine dioxide.⁷ We found that the addition of catalytic amounts of 2,2,5,5-tetramethyl-4-phenyl-3-imidazolin-1-oxyl 3-oxide accelerates the reaction (see Table 1). However, the effect of the iminoxyl radical is much less pronounced in this case than in 1,3-dioxacycloalkane oxidation with oxone.⁸

Table 1. Composition and yields of the products of oxidation of 1,3-dioxanes 7–9 (DH) with chlorine dioxide (MeCN, 35 °C)

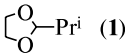
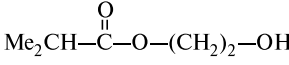
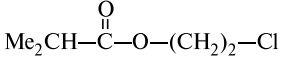
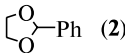
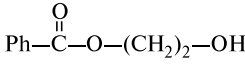
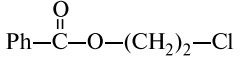
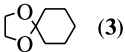


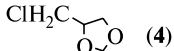
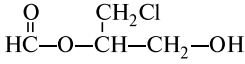
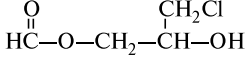
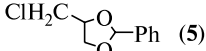
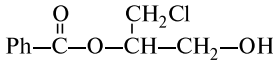
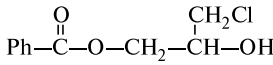
DH	Time/h	Products	Yield ^a (%) at DH : ClO ₂ ^b		
			1 : 1	1 : 3	1 : 3 ^c
 (7)	6		24	60	75
			12	30	25
 (8)	4		27	46	53
			14	23	27
		PhCOOH	1	—	1
 (9)	4		16	24	60
		PhCOOH	6	4	4

^a The product yield based on the starting DH.

^b Molar ratio.

^c Oxidation in the presence of 2,2,5,5-tetramethyl-4-phenyl-3-imidazolin-1-oxyl 3-oxide (DH : >N—O[•] = 1 : 0.01 mol mol⁻¹).

Table 2. Composition and yields of the oxidation products of 1,3-dioxolanes 1–5 (DH) with chlorine dioxide (MeCN, 35 °C)

DH	DH : ClO ₂ /mol mol ⁻¹	Time /h	Products	Yield* (%)
 (1)	1 : 3	4		46
				29
 (2)	1 : 3	4		61
				24
			PhCHO	1
			PhCOOH	2
 (3)	1 : 3	12		82
				7
 (4)	1 : 3	7		11
				20
 (5)	1 : 3	4		20
				11
			PhCHO	27

* Product yield based on the starting DH.

Reaction kinetics. The kinetics of the reaction of ClO₂ with 1,3-dioxacycloalkanes was studied by monitoring chlorine dioxide with the condition [ClO₂]₀ ≪ [DH]₀, where [ClO₂]₀ and [DH]₀ are the starting concentrations of chlorine dioxide and the substrate, respectively. Typical kinetic curves for the consumption of ClO₂ are described by a first-order equation with a high correlation coefficient ($r \approx 0.980\text{--}0.999$) (Fig. 1).

The linearized kinetic curves were used to calculate the apparent pseudo-first-order rate constants $k_{\text{app}} = k \cdot [\text{DH}]^n$ (k is the second-order rate constant, n is the order of the reaction with respect to DH). The linear dependence of k_{app} on the concentration of 1,3-dioxacycloalkanes ($r > 0.99$) implies the first order with respect to DH (Fig. 2).

Thus, the kinetic equation of the reaction has the form

$$-d[\text{ClO}_2]/dt = k \cdot [\text{ClO}_2] \cdot [\text{DH}].$$

For all 1,3-dioxacycloalkanes studied, the temperature dependence of the second-order rate constant was

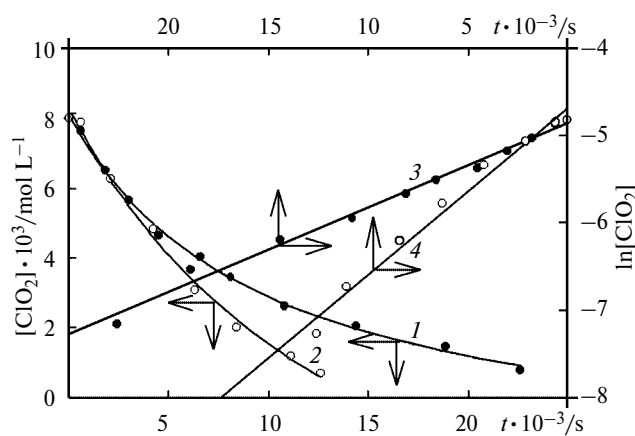


Fig. 1. Typical kinetic curves for the consumption of ClO₂ in the reactions with 1,3-dioxanes (1, 2) and their linearization in semilogarithmic coordinates (3, 4): 4-methyl-1,3-dioxane (6) (1, 3), 2-isopropyl-4-methyl-1,3-dioxane (7) (2, 4) ([ClO₂]₀ = 8 · 10⁻³ mol L⁻¹, [DH]₀ = 0.8 mol L⁻¹, MeCN, 61 °C).

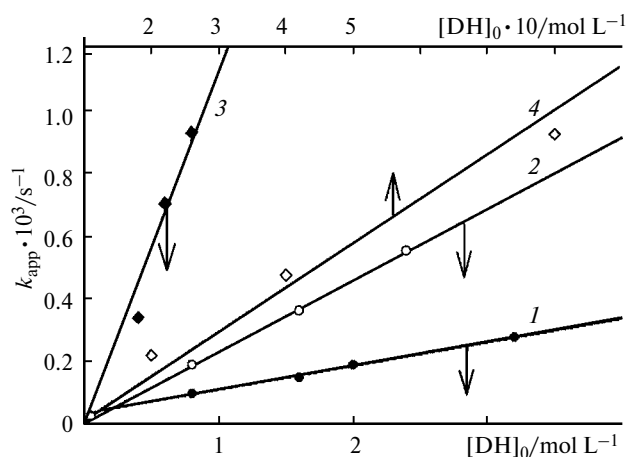


Fig. 2. Apparent rate constant for the oxidation of 1,3-dioxanes with chlorine dioxide (k_{app}) vs. the concentration of 1,3-dioxanes **6** (**1**), **7** (**2**), **8** (**3**), **9** (**4**) ($[\text{ClO}_2]_0 = (4\text{--}8) \cdot 10^{-3} \text{ mol L}^{-1}$, $[\text{DH}]_0 = 0.2\text{--}3.2 \text{ mol L}^{-1}$, MeCN, 61 °C).

measured and the activation parameters were determined (Table 3).

According to the data of Table 3, an increase in the activation entropy is accompanied by an increase in the activation enthalpy, *i.e.*, a compensation effect is observed (Fig. 3).

$$\Delta H^\ddagger_{298} = (105.7 \pm 3) + (0.37 \pm 0.03) \cdot \Delta S^\ddagger_{298} \quad (r = 0.99)$$

The presence of the compensation effect attests, apparently, to a single reaction mechanism for all of the 1,3-dioxacycloalkanes.

The influence of the solvent nature on the apparent rate constant for the consumption of chlorine dioxide in the reaction with 2-isopropyl-1,3-dioxolane (**1**) was studied in the following solvents: MeCN, CCl_4 , benzene, acetone, AcOEt, EtOH, and MeOH. It was found that the nature of the solvent has a slight influence on the k_{app}

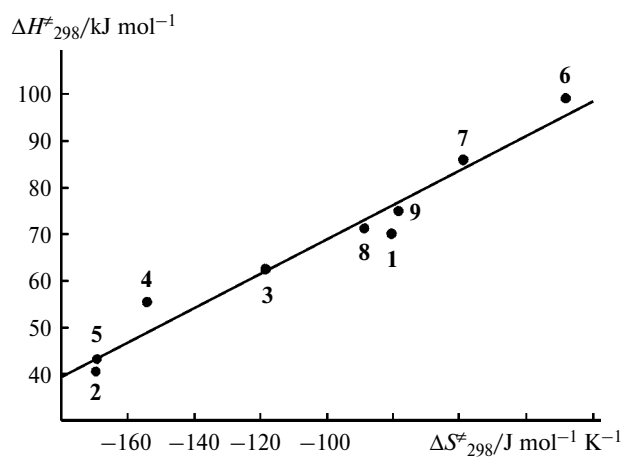
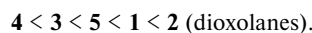
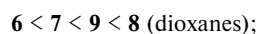


Fig. 3. Activation enthalpy (ΔH^\ddagger_{298}) vs. activation entropy (ΔS^\ddagger_{298}) for the reaction of 1,3-dioxacycloalkanes **1–9** with chlorine dioxide.

value (Table 4), which is indicative of low polarity of the transition state of the rate-limiting step.

The results obtained provide the conclusion that the reactivity of the compounds under study varies in the following sequence:



The composition of the reaction products (see Tables 1 and 2) and the kinetic data indicate that the C(2)—H bond is attacked predominantly in the reaction of 1,3-dioxacycloalkanes with ClO_2 . The introduction of an alkyl (compounds **1**, **2**, **5**, **7–9**) or, the more so, a phenyl (compounds **2**, **5**, **8**, **9**) groups into position 2 of the substrate decreases the strength of the tertiary C—H bond, which, in turn, results in a higher reactivity toward chlorine dioxide. Indeed, for compounds **6** and **7**, $k \cdot 10^4 = 0.07$ and $0.28 \text{ L mol}^{-1} \text{ s}^{-1}$ (40.5 °C); for compounds **6** and **8**,

Table 3. Activation parameters of the reaction of chlorine dioxide with 1,3-dioxacycloalkanes (DH) at 25 °C

DH	Solvent	$k \cdot 10^4$ / $\text{L mol}^{-1} \text{ s}^{-1}$	E_a / kJ mol^{-1}	$\log A$	ΔH^\ddagger_{298} / kJ mol^{-1}	$-\Delta S^\ddagger_{298}$ / $\text{J mol}^{-1} \text{ K}^{-1}$
1	CCl_4	1.90	73.4	9.0	69.9	80.3
2	CCl_4	8.28	42.7	4.4	40.2	169.4
3	CCl_4	0.43	64.8	7.0	62.3	118.4
4	CCl_4	0.12	57.7	5.2	55.2	154.0
5	CCl_4	2.50	45.6	4.4	43.1	169.2
6	MeCN	0.01	101.7	11.79	99.1	27.8
7	MeCN	0.05	88.3	10.2	85.8	58.6
8	MeCN	0.49	73.6	8.6	71.1	88.7
9	MeCN	0.03	77.4	9.1	74.9	78.2

Note. k is the second-order rate constant, E_a is the activation energy, A is the pre-exponential factor in the Arrhenius equation, ΔH^\ddagger_{298} and ΔS^\ddagger_{298} is the activation enthalpy and entropy, respectively.

Table 4. Solvent effect on the oxidation rate of 2-isopropyl-1,3-dioxolane (**1**) with chlorine dioxide (22 °C, [ClO₂]₀ = 1.44 · 10⁻² mol L⁻¹, [DH]₀ = 1.14 mol L⁻¹)

Solvent	ϵ	$k_{\text{app}} \cdot 10^4 / \text{s}^{-1}$
CCl ₄	2.2	1.50 ± 0.02
C ₆ H ₆	2.3	2.11 ± 0.03
AcOEt	6.7	0.97 ± 0.01
MeC(=O)Me	20.7	1.70 ± 0.04
EtOH	24.3	2.01 ± 0.02
MeOH	32.7	0.75 ± 0.04

Note. ϵ is the dielectric constant of the medium, k_{app} is the apparent rate constant.

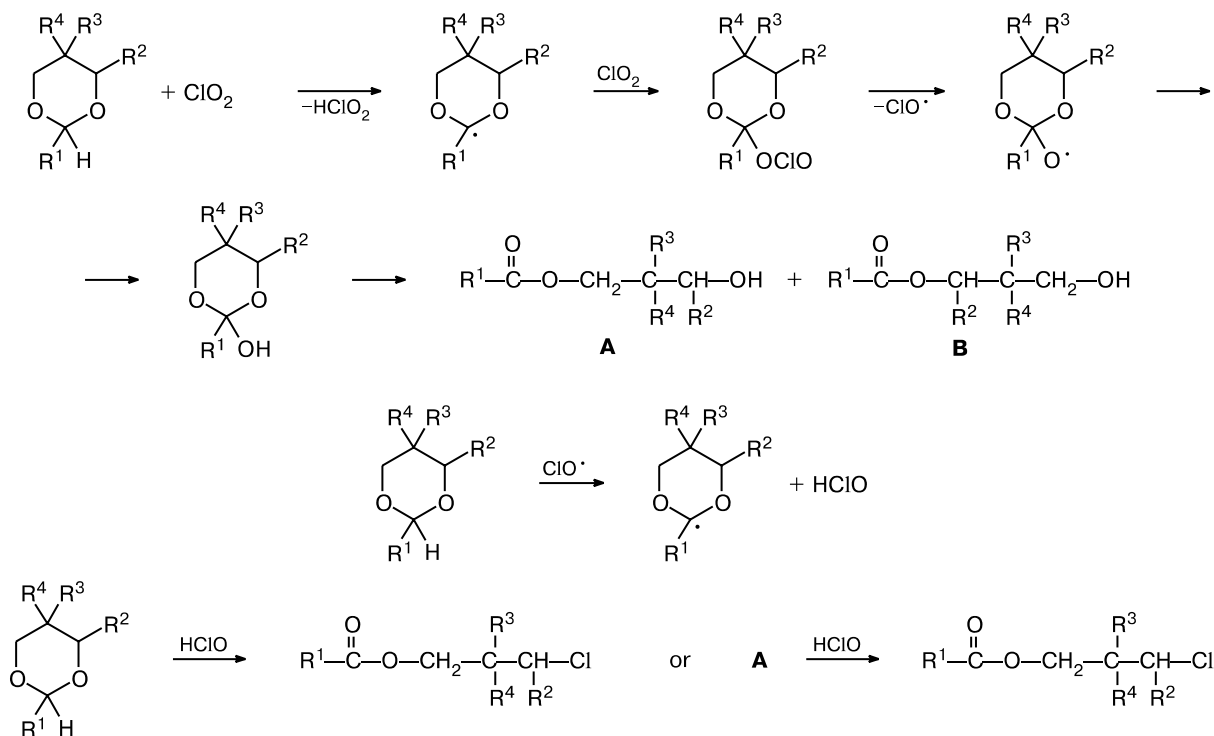
$k \cdot 10^4 = 0.31$ and $4.51 \text{ L mol}^{-1} \text{ s}^{-1}$ (51 °C); for compounds **4** and **5**, $k \cdot 10^4 = 0.25$ and $6.4 \text{ L mol}^{-1} \text{ s}^{-1}$ (40 °C), respectively.

In view of the fact that solvent polarity has a slight influence on the oxidation rate of 1,3-dioxacycloalkanes with chlorine dioxide under the experimental conditions and by comparing the second order rate constants for the reaction of 1,3-dioxanes and 1,3-dioxolanes at the same temperature (see Table 3), one can conclude that 1,3-dioxanes are more stable against chlorine dioxide than 1,3-dioxolanes. The difference between five- and six-membered rings is explained by conformational properties of the molecules.⁹ The introduction of substituents

into 1,3-dioxane results in fixation of the chair conformation in such a way that the C—H bond to be attacked occurs in a conformation favorable for the reaction, because it has an antiperiplanar orientation with respect to the orbitals of the oxygen lone electron pairs. The five-membered ring does not have a clear-cut conformational minimum; therefore, the steric effect of the substituents in position 2 is less pronounced.¹⁰ The introduction of Me groups into the fourth or fifth position of 1,3-dioxacycloalkanes changes insignificantly the susceptibility of compounds for oxidation compared to the unsubstituted analogs.^{11,12} These trends are observed in the oxidation of 1,3-dioxacycloalkanes with ozone,⁹ molecular oxygen,¹³ and dimethyldioxirane.^{11,12}

The results of the study of the products and kinetics of the reaction of ClO₂ with 1,3-dioxacycloalkanes, together with published data on the oxidation of hydrocarbons with chlorine dioxide^{14,15} and cyclic acetals with nitrogen dioxide¹⁶ allowed us to propose a reaction scheme that accounts for the products and kinetics observed. Chlorine dioxide containing an unpaired electron attacks the C—H bond adjoining the O atom to give an alkyl radical. The radical reacts with ClO₂ to give the reaction products (Scheme 2). The accumulation of benzaldehyde and benzoic acid upon the oxidation of cyclic acetals containing a phenyl substituent in position 2 is due to an attack by ClO₂ on the C(4) atom. The accumulation of the chlori-

Scheme 2



nation products can be due to the action of hypochlorous acid formed during oxidation.

References

1. D. L. Rakhmankulov, R. A. Karakhanov, S. S. Zlotskii, E. A. Kantor, U. B. Imashev, and A. M. Syrkin, *Khimiya i tekhnologiya 1,3-dioksatsiklanov* [Chemistry and Technology of 1,3-Dioksacyclanes], in *Itogi nauki i tekhniki. Ser. Tekhnologiya organicheskikh veshchestv* [Advances in Sciences and Engineering. Ser. Technology of Organic Compounds], 1979, **5**, 288 pp.
2. E. M. Kuramshin, V. K. Gumerova, V. A. D'yachenko, L. G. Kulak, M. A. Molyavko, M. V. Kochinashvili, A. F. Mufteev, S. S. Zlotskii, and D. L. Rakhmankulov, *Zh. Obshch. Khim.*, 1988, **58**, 1069 [*J. Gen. Chem. USSR*, 1988, **58** (Engl. Transl.)].
3. *Handbuch der preparativen anorganischen Chemie in drei Banden*, Herausgegeben von G. Brauer, Stuttgart, 1975.
4. A. J. Gordon and R. A. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, Wiley, New York—London—Sydney—Toronto, 1972.
5. P. L. Anelli, S. Banfi, F. Montanary, and S. Quici, *J. Org. Chem.*, 1989, **54**, 2970.
6. T. P. Vorob'eva, E. L. Durova, and Yu. N. Kozlov, *Zh. Fiz. Khim.*, 1977, **51**, 2686 [*Russ. J. Phys. Chem.*, 1977, **51** (Engl. Transl.)].
7. I. M. Ganiev, Q. K. Timerghazin, A. F. Khalizov, V. V. Shereshovets, A. I. Grigor'ev, and G. A. Tolstikov, *J. Phys. Org. Chem.*, 2001, **14**, 38.
8. Z. F. Akbalina, N. N. Kabal'nova, S. S. Zlotsky, I. A. Grigoriev, V. V. Shereshovets, and G. A. Tolstikov, *React. Kinet. Lett.*, 2001, **72**, 147.
9. B. M. Brudnik, E. M. Kuramshin, A. I. Naimushin, S. S. Zlotskii, and D. L. Rakhmankulov, *Zh. Organ. Khim.*, 1982, **18**, 1807 [*J. Org. Chem. USSR*, 1982, **18** (Engl. Transl.)].
10. D. L. Rakhmankulov, E. M. Kuramshin, and S. S. Zlotskii, *Usp. Khim.*, 1985, **54**, 923 [*Russ. Chem. Rev.*, 1985, **54** (Engl. Transl.)].
11. G. M. Abushakhmina, N. N. Kabal'nova, S. S. Zlotsky, V. V. Shereshovets, and D. L. Rakhmankulov, *React. Kinet. Catal. Lett.*, 1999, **67**, 289.
12. Z. F. Akbalina, Ph.D. Thesis (Chem.), Ufa State Petroleum Technical University, Ufa, 2000, 117 pp. (in Russian).
13. L. G. Kulak, S. S. Zlotskii, E. M. Kuramshin, and D. L. Rakhmankulov, *Bashkir. Khim. Zh.*, 1995, **2**, 13.
14. B. O. Lindgren, C. M. Svan, and G. Widmark, *Acta Chem. Scand.*, 1965, **19**, 7.
15. P. S. Fredricks, B. O. Lindgren, and O. Theander, *Acta Chem. Scand.*, 1970, **24**, 736.
16. T. Nishiguchi, T. Ohosima, A. Nishida, and Sh. Fujisaki, *J. Chem. Soc., Chem. Commun.*, 1995, 1121.

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