LITERATURE CITED

1. H. D. Scharf and E. Wolters, Chem. Ber., 111, 639 (1978).
2. N. V. Kuznetsov and R. A. Myrsina, Ukr. Khim. Zh., 36, 1050 (1970).
3. J. Mattay, W. Thünher, and H. D. Scharf, Ann. Chem., No. 6, 1105 (1981).
4. A. A. Petrov, Zh. Obshch. Khim., 15, 931 (1945).
5. M. Makosha and M. Fedorinski, Zh. Vses. Khim. Ova., 24, 466 (1979).

THE LIQUID-PHASE FREE RADICAL ISOMERIZATION OF CYCLIC DIMETHYLFORMAMIDE ACETALS

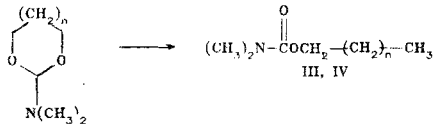
E. V. Pastushenko, D. Kurbanov, S. S. Zlotskii, and D. L. Rakhmankulov

UDC 547.787'841:541.515:542.952.1

In the presence of tert-butyl peroxide, 2-dimethylamino-1,3-dioxacyclanes are converted to esters of dimethylcarbamic acid. The reaction is described by a kinetic equation for an unbranched chain reaction with quadratic chain termination. The five-membered heterocycle is more reactive than the six-membered heterocycle. The predominant site for free radical attack is the methine group adjacent to the three heteroatoms.

In our previous work [1-3], we showed that cyclic acetals of aliphatic aldehydes are converted in the presence of free radical donors to the isomer esters. Under analogous conditions, the corresponding carbonates and their derivatives are formed from 2-alkoxy-1,3-dioxacyclanes and their analogs [4, 5]. In order to investigate the effect of ring size and the nature of substituents on this reaction, we studied the kinetics of the liquid-phase radical isomerization of cyclic acetals of dimethylformamide induced by tert-butyl peroxide (TBP).

2-Dimethylamino-1,3-dioxacyclanes I and II are converted to the isomeric dimethylcarbamate esters III and IV with an initial rate V_{ef}. The $V_{ef}/\sqrt{V_{TBA}}$ (V_{TBA} is the rate of formation of tert-butyl alcohol in the system which reflects the initiation rate) remains satisfactorily invariant in the PTB concentration range from 0.05 to 0.5 mole/liter (Table 1). Hence, esters III and IV are formed by an unbranched radical chain mechanism with quadratic chain termination



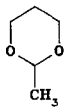
I, II — I, III n= 0; II, IV n= 1

The value for V_{ef} increases linearly with increasing substrate concentration, while the rate of formation of tert-butyl alcohol (V_{TBA}) remains constant (Fig. 1). This linear increase indicates the participation of one acetal molecule in the rate-limiting step of the isomerization. The invariance of V_{TBA} indicates that all the tert-butoxyl radicals are completely consumed in the hydrogen abstraction step at acetal concentrations greater than 2.0 mole/liter. The lines giving the dependence of V_{ef} on the substrate concentration passes through the origin. Thus the rearrangement of the cyclic radical to a linear radical is not the slow step in the ester formation. These experimental results and our previous data [1, 4] indicate that acetals I and II isomerize according to our previously proposed mechanism [1]:

Ufa Petroleum Institute, Ufa 450062. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1614-1617, December, 1983. Original article submitted January 3, 1983.

0009-3122/83/1912-1273$07.50

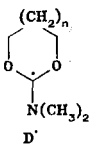
TABLE 1. Dependence of the Initial Rate of Ester Formation V_{ef} and of tert-Butyl Alcohol Formation V_{TBA} on the tert-Butyl Peroxide Concentration at 130°C

Compound	Initial concentrations, mole/liter		$V_{ef} \cdot 10^4$	$V_{TBA} \cdot 10^4$	$\nu = \frac{V_{ef}}{V_{TBA}}$	$\frac{V_{ef}}{\sqrt{V_{TBA}}} \cdot 10^2$	$\frac{k_3}{\sqrt{k_4}} \cdot 10^3$
	acetal	TBA	mole/liter·sec			(mole/liter·sec)$^{1/2}$	
I	8,1	0,05	0,12	0,03	4,0	0,7	1,4±0,2
		0,1	0,17	0,05	3,4	0,8	
		0,2	0,23	0,10	2,3	0,7	
		0,2	0,28	0,16	1,8	0,7	
		0,5	0,38	0,26	1,5	0,7	
II	7,6	0,05	0,06	0,02	3,0	0,4	0,8±0,1
		0,1	0,09	0,04	2,3	0,4	
		0,2	0,13	0,09	1,4	0,4	
		0,3	0,17	0,14	1,2	0,5	
		0,5	0,22	0,29	0,9	0,5	
*	11,1	0,3	3,8	0,4	8,4	5,7	7,0
							
*	9,6	0,3	0,6	0,2	3,0	1,3	1,8
							

*From our previous work [1].

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{k_i} 2\,(CH_3)_3CO^{\cdot} \quad (0)$$

$$I,II + (CH_3)_3CO^{\cdot} \xrightarrow{k_1} (CH_3)_3COH + \text{D}^{\cdot} \quad (1)$$

D$^{\cdot}$: 

$$D^{\cdot} \xrightarrow{k_2} (CH_3)_2N-\overset{O}{\overset{\|}{C}}-OCH_2-(CH_2)_n-\dot{C}H_2 \quad (2)$$

$$\dot{E} + I,II \xrightarrow{k_3} III,IV + D^{\cdot} \quad (3)$$

$$2\,\dot{E} \xrightarrow{k_4} \text{molecular products} \quad (4)$$

Since $k_i[TBP] = 0.5V_{TBA}$ and the disproportionation of the alkyl radicals $\dot{E}$ may be neglected [1], the isomerization rate is described by the equation

$$V_{ef} = \frac{k_3}{\sqrt{k_4}} \cdot [I, II] \cdot \sqrt{0{,}5V_{TBA}}$$

A study of the isomerization of I in the range from 120° to 150°C gave the activation energies and preexponential terms for the formation of ester III and decomposition of TBP (Table 2).

Comparison of $k_3/\sqrt{k_4}$ values at 130°C indicates that the reactivity of acetal II is less than that of I. This finding is in good accord with our previous data on the enhanced stability of six-membered heterocycles (tetrahydropyran and 1,3-dioxane) in radical reactions in comparison to their five-membered analogs [1]. This discrepancy is apparently a factor of the reduced advantage in going from sp^3 hybridization at $C_{(2)}$ to sp^2 for six-membered rings.

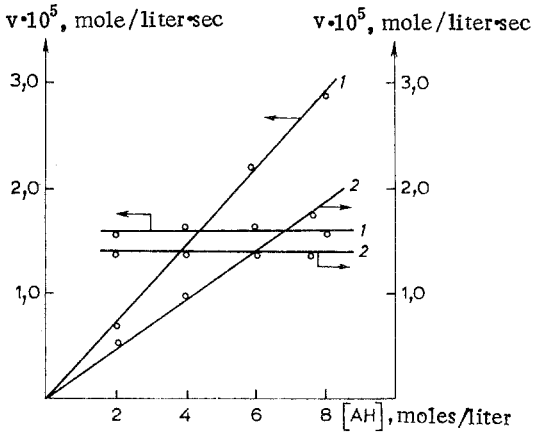


Fig. 1. Dependence of the initial rate of ester formation V_{ef} and of tert-butyl alcohol V_{TBA} on the acetal concentration in chlorobenzene at 130°C, [TBP] = 0.3 mole/liter: 1) isomerization of acetal I and 2) isomerization of acetal II.

Dioxacyclanes I and II are about five times less reactive than the corresponding cyclic acetals of acetaldehyde [1]. This apparently may be attributed to the fact that the dimethylamino group, in contrast to the methyl group, occupies pseudoaxial and axial positions in I and II and the free radicals attack the equatorial $C_{(2)}$—H bonds which, according to Beckwith and Easton [6], are stronger than the axial bonds.

The experimentally determined isomerization activation energy (Table 2) is the difference between the activation energy for chain propagation (ΔE_3) and one-half of the activation energy for the termination reaction (ΔE_4):

$$\Delta E_3 - 0{,}5\Delta E_4 \text{ (Table 2).}$$

Ė radicals, similar to alkyl radicals, have recombination activation energy of about 1.0 kcal/mole [1], which permits us to estimate ΔE_3 = 15.8 kcal/mole, which is about 4 kcal/mole greater than the activation energy for hydrogen abstraction from 2-alkyl-1,3-dioxolanes by alkyl radicals [1].

On the whole, oxygen and carbon radicals generally attack the methine group adjacent to the three heteroatoms in I and II. This was found in preparative runs, in which the selectivity for the formation of esters III and IV is not less than 80% for 30-40% conversion of the starting compounds (Table 3).

EXPERIMENTAL

Samples of the initial 2-dimethylamino-1,3-dioxacyclanes I and II were obtained by reported methods [7]. The purity of substrates I and II and of the initiator were monitored chromatographically and was not less than 98%. The products of the conversions of III and IV

TABLE 2. Kinetic Parameters for the Isomerization of 2-Dimethylamino-1,3-dioxolane

T, °C	$k_3/\sqrt{k_4} \cdot 10^3$ (liter/mole·sec)$^{1/2}$	$k_i \cdot 10^5$ sec^{-1}	$\Delta E_{ef} = \Delta E_3 - 0{,}5\Delta E_4$	ΔE_3	ΔE_i
			kcal/mole		
120	0,9	2,0			
130	1,4	5,3			
140	2,6	16,0	15,3±0,3	15,8±0,3	36,2±1,5
150	4,2	50,0			

TABLE 3. Isomerization of Dimethylformamide Acetals Initiated by tert-Butyl Peroxide in Chlorobenzene at 140°C for 3 h, [TBP] = 0.6 mole/liter

Acetal	Concentration, mole/liter		Ester concentration mole/liter	Acetal conversion, %	Selectivity of of ester formation, %
	initial	final			
I	3,0	1,8	III 1,0	40	83
II	3,0	2,1	IV 0,7	30	77

were separated from the reaction mixture on a PAKhV-08 preparative chromatograph using a column 3 m in length and 8 mm in diameter packed with 25% SKTFT-50 on Chromaton NAW with helium gas carrier, 70-150°C column temperature and 150°C injector temperature. The reaction products were identified relative to their PMR spectra and by gas-liquid chromatography by comparison of retention times with authentic samples. The spectral measurements were taken on UR-20 and Tesla BS-497 spectrometers.

The kinetic experiments were carried out in thermostatted ampuls which were thoroughly bubbled with argon after filling with a solution of the substrate and tert-butyl peroxide. The isomerization of dimethylformamide acetals I and II was found not to proceed without the presence of initiator.

The concentration of the products was determined chromatographically by the internal standard method. The analysis was carried out on an LKhM-8MD chromatograph with flame ionization detector and a column 3 m in length and 3 mm in diameter, helium gas carrier, 1 liter/h flow rate, 4 deg/min temperature rise rate, and 150°C injector temperature. The internal standard was 0.1 mole/liter isooctane in chlorobenzene.

2-N,N-Dimethylamino-1,3-dioxolane (I). Bp 142-143°C, d_4^{20} 1.007. PMR spectrum (CCl_4, HMDS internal standard): 2.83 [s, 6H, $(CH_3)_2N$], 3.76 (m, 4H, ring OCH_2), 4.14 ppm (s, 1H, $HC\langle$).

2-N,N-Dimethylamino-1,3-dioxane (II). Bp 81°C (32 mm), d_4^{20} 1.000. PMR spectrum: 1.11-1.38 (m, 2H, ring CH_2), 2.20 [s, 6H, $(CH_3)_2N$], 3.52-4.08 (m, 4H, ring CH_2O), 4.54 ppm (s, 1H, $HC\langle$).

Ethyl Ester of Dimethylcarbamic Acid (III). Bp 146°C, d_4^{20} 0.970. PMR spectrum: 1.2 (t, 3H, CH_3), 2.83 [s, 6H, $(CH_3)_2N$], 3.55 ppm (q, 2H, OCH_2).

Propyl Ester of Dimethylcarbamic Acid (IV). Bp 160-162°C, d_4^{20} 0.953. PMR spectrum: 0.92 (t, 3H, CH_3), 1.35-1.9 (2H, CH_2), 2.83 [s, 6H, $(CH_3)_2N$], 3.50 ppm (t, 2H, OCH_2).

LITERATURE CITED

1. É. Kh. Kravets, S. S. Zlotskii, V. S. Martem'yanov, and D. L. Rakhmankulov, Khim. Geterotsikl. Soedin., No. 9, 1171 (1976).
2. D. L. Rakhmankulov, R. A. Karakhanov, S. S. Zlotskii, E. A. Kantor, U. B. Imashev, and A. M. Syrkin, in: Progress in Science and Technology [in Russian], Vol. 5, Moscow (1979), p. 134.
3. D. L. Rakhmankulov and S. S. Zlotskii, Khim. Geterotsikl. Soedin., No. 8, 1011 (1977).
4. L. L. Kostyukevich, E. V. Pastushenko, S. S. Zlotskii, and D. L. Rakhmankulov, Dokl. Akad. Nauk SSSR, 265, 1177 (1982).
5. A. L. Lashova, V. V. Zorin, S. S. Zlotskii, and D. L. Rakhmankulov, Khim. Geterotsikl. Soedin., No. 5, 701 (1981).
6. A. Beckwith and C. Easton, J. Am. Chem. Soc., 103, 615 (1981).
7. V. V. Mezheritskii, E. P. Olekhnovich, S. M. Luk'yanov, and G. N. Dorofeenko, Orthoesters in Organic Synthesis [in Russian], Izd. Rostovsk. Univ. (1976).