1,4-DIOXANES AS PRODUCTS OF THE OXIDATION OF N-VINYLLACTAMS

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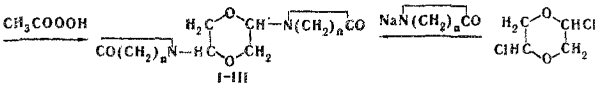
2,5-Disubstituted 1,4-dioxanes have been obtained by the oxidation of N-vinyllactams, represented by N-vinylpyrrolidone, N-vinylpiperidone, and N-vinylcaprolactam, and their structure has been shown by independent synthesis: the reaction of trans-2,5-dichloro-1,4-dioxanes with alkali-metal salts of the lactams also gave 2,5-di(N-2-oxopolymethyleneimino)-1,4-dioxanes.

Substances simultaneously including an α-oxide and a lactam ring are of undoubted interest for the synthesis of new polyesters and as potential physiologically active agents. In order to obtain N-epoxyethyllactams we have studied the oxidation of N-vinyllactams. There is no information in the literature on the oxidation of a vinyl group directly attached to the nitrogen atom of a lactam ring. There is a patent statement [1] of the possibility of oxidizing N-vinylcaprolactam to N-epoxyethylcaprolactam. However, no information on the experimental conditions or the constants of the substance are given. So far as concerns the oxidation of a vinyl group attached to other heteroatoms, there is only brief and contradictory information in the literature. Thus, by oxidizing vinyl ethyl ether, Bergman [2, 3] obtained a product to which, on the basis of a molecular weight determination, he assigned the structure of 1,4-dioxane. On repeating the reaction, Dedusenko and Movsumzade obtained neither an α-oxide nor its dimer [4]. It has been shown in a number of papers that the oxidation of the double bond of vinyl ethers leads only to the formation of by-products [5, 6]. The most reliable information relates only to the synthesis of oxides from vinylsilanes [7].

In the present work, the oxidation of N-vinylpyrrolidone, N-vinylpiperidone, and N-vinylcaprolactam was performed with peracetic acid in diethyl ether or methylene chloride. The crystalline products obtained possessed a doubled molecular weight as compared with the α-oxides and, it may be assumed, were their dimers:



I–III

I n = 3; II n = 4; III n = 5

The compounds isolated decomposed in an acid medium with the formation of glycolaldehyde, which was identified in the form of the oxazone. Decomposition of this type confirms the presence of a dioxane structure [8, 9]. Preliminary results of an X-ray structural analysis of the oxidation product of N-vinylcaprolactam also does not contradict a dioxane structure. It is likely that the lactam α-oxides formed readily dimerize in an acid medium with the formation of 1,4-dioxanes. Similar processes are known in the literature for ethylene oxide [10, 11], propylene oxide [12], styrene oxide [13], and others. The structure of the products obtained by the oxidation of the N-vinyllactams was shown definitively by independent synthesis from trans-2,5-dichloro-1,4-dioxane and the alkali-metal salts of the lactams. The cause of the low yields of the 1,4-dioxanes obtained by this method is pronounced resinification. The identity of the compounds obtained by the two methods was established by their IR spectra (Figs. 1 and 2) and melting points; mixtures gave no depression of the melting points. It may be assumed that the 2,5-disubstituted dioxanes have the trans configuration, since, according to the literature [14, 15], the initial 2,5-dichlorodioxane is trans-2,5-dichloro-1,4-dioxane.

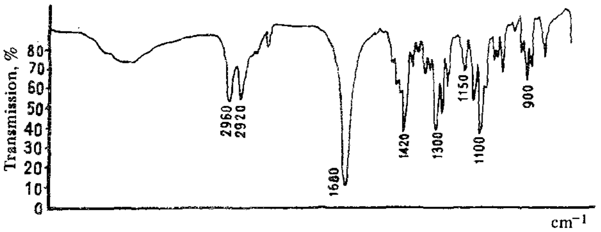


Fig. 1. IR spectrum of 2,5-di(N-2-oxohexamethyleneimino)-1,4-dioxane (III) obtained by method A.

In the oxidation of the N-vinyllactams, the yield of 1,4-dioxanes depends on the size of the lactam ring. Thus, in the oxidation of N-vinylpyrrolidone, the yield amounted to 70%, in the case of N-vinylcaprolactam it fell to 20%, and for N-vinylpiperidone it did not exceed 10%. About 25 days is required for the complete reaction, but the bulk of the 2,5-di(N-2-oxotetramethyleneimino)-1,4-dioxane (I) is formed in the first 10 days. A study of the reaction mixture by thin-layer chromatography showed that in addition to the 1,4-dioxanes it contains unchanged vinyllactam and decomposition products, lactams and glycolaldehyde. In the oxidation of N-vinylcaprolactam and N-vinylpiperidone, large amounts of resinous products were formed from which it was impossible to isolate individual substances.

EXPERIMENTAL

A. trans-2,5-Di(N-2-oxotetramethyleneimino)-1,4-dioxane (I). In drops, a solution of 23.7 g (0.31 mole) of peracetic acid (in the form of the 80% acid) in 160 ml of absolute diethyl ether was added to a solution of 33.3 g (0.30 mole) of N-vinylpyrrolidone in 150 ml of absolute diethyl ether cooled to −20° C, and the mixture was kept at −10° C for 2 hr, at −2 to −5° C for 18 hr, and then at room temperature.

trans-2,5-Di(N-2-oxopolymethyleneimino)-1,4-dioxanes (I–III)

Compound	Mp, °C	R_f	Empirical formula	Found				Calculated				Yield, %*	
				M	%			M	%			A	B
					C	H	N		C	H	N		
I	219—220	0.8312	$C_{12}H_{18}N_2O_4$	247**	56.44	7.16	11.15	254.3	56.64	7.13	11.00	70	5
II	252—253	0.8351	$C_{14}H_{22}N_2O_4$	258***	59.25	7.93	9.60	—	59.55	7.85	9.91	10	3
III	247—248	0.8385	$C_{16}H_{26}N_2O_4$	299.8**	61.59	8.39	8.93	310.4	61.84	8.44	9.03	20	3

*A) by the oxidation of vinyllactam; B) from dichlorodioxane.
**By reversed ebullioscopy.
***By ebullioscopy.

White lustrous crystals gradually deposited. They were separated off, washed with acetone, and dried. After 26 days, 28.3 g (70%) had been obtained, mp 219–220° C (from water). By thin-layer chromatography on Al_2O_3 of activity grade II in the acetone (40 ml)–water (one drop) system, the filtrate was found to contain vinylpyrrolidone (R_f = 0.88), pyrrolidone (R_f = 0.45), glycolaldehyde, and trans-2, 5-di(N-oxotrimethyleneimino)-1, 4-dioxane (R_f = 0.83).

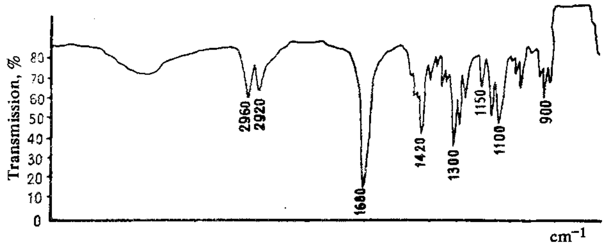


Fig. 2. IR spectrum of 2,5-di(N-2-oxohexamethyleneimino)-1,4-dioxane (III) obtained by method B.

Compounds II and III were obtained similarly.

B. Independent synthesis of compounds I–III. With stirring, 0.02 mole of trans-2,5-dichlorodioxane [16, 17] in 55 ml of xylene was added in drops to 0.04 mole of the sodium salt of a lactam, obtained from the lactam and metallic sodium in 25 ml of xylene. The reaction mixture was left at room temperature for 72 hr. The precipitate was filtered off and extracted several times with methylene chloride. From the extracts I, II, and III were isolated, and they were purified by two reprecipitations from methylene chloride with diethyl ether.

Hydrolysis of I–III in an acid medium. To a boiling solution of 3 g of 2,4-dinitrophenylhydrazine in 50 ml of 10% hydrochloric acid was added 2.5 g (0.05 mole) of I. The osazone that deposited was washed with water and recrystallized from pyridine. This gave 0.06 g of glycolaldehyde osazone, mp 331–332° C (decomp) [18]. R_f = 0.37 (Al_2O_3 of activity grade II, petroleum ether–diethyl ether [1 : 2] system). Found, %: C 40.40; H 2.53; N 26.30. Calculated for $C_{14}H_{18}O_4N_8$, %: C 40.21; H 2.41; N 26.79.

X-Ray structural analysis of trans-2,5-(N-2-oxohexamethyleneimino)-1,4-dioxane (III). Crystals monoclinic, space group 2 1/a; cell parameters: a = 12.28 ± 0.10 Å; b = 793 Å^3 (volume of the cell); c = = 11.09 ± 0.3; C = 5.87 ± 0.06; $d_{m,m}$ = 1.261/cm^3; β = 94.1 ± 10.

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