RADICAL TELOMERIZATION OF 1-HEXENE BY 1,4-DIOXANE

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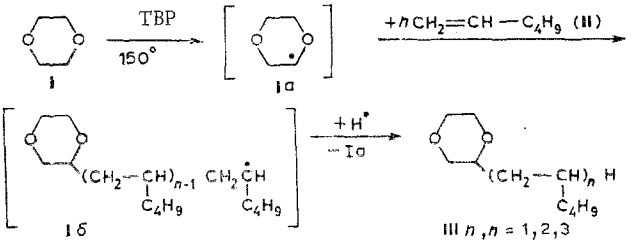
It was established that telomer homologs of a number of 2-alkyl-1,4-dioxanes are formed as a result of radical telomerization of 1-hexene by 1,4-dioxane. The partial chain-propagation constants of the process were calculated, and the mass spectra of the reaction products were studied.

Numerous studies [1, 2] have been devoted to reactions involving the radical telomerization of lower olefins by various organic compounds. However, virtually no information regarding the telomerization of unsaturated hydrocarbons by cyclic ethers is available.

We have established that telomer homologs of a series of 2-alkyl-1,4-dioxanes (III_n) are formed as a result of telomerization of 1-hexene (II) by 1,4-dioxane (I) initiated by tert-butyl peroxide (TBP):



Cyclic radical Ia evidently adds to the carbon—carbon double bond of monomer II, and the growing macroradicals (Ib), due to chain propagation to telogen I, form compounds of the III_n series: hexyl-1,4-dioxane (III_1), (2-butyl)octyl-1,4-dioxane (III_2), and (2,4-dibutyl)-decyl-1,4-dioxane (III_3). The overall yield of the identified III_n (n = 1, 2, 3) reaches 85% based on the converted olefin (Table 1).

As the amount of olefin is increased, the percentage of higher homologs III_n ($n > 3$) in the reaction mixture increases vis-à-vis a simultaneous decrease in the fraction of the lower homologs ($n \leqslant 3$, Table 2). The partial chain-propagation constants (C_n) calculated by the method in [3] are low [$C_1 = 0.41$, $C_2 = 0.23$, and $C_3 = 0.23$ (Table 2)], from which it follows that in the reaction with 1-hexene, 1,4-dioxane as a chain propagator is close in its efficiency to 1,3-dioxacyclanes [4] and carboxylic acids and their esters [1]. The low C_n values show that the growing radicals react more readily with the olefin than with the telogen.

Products III_1 and III_2 were isolated from the reaction mixture by preparative gas-liquid chromatography (GLC), and their structures were established by PMR and chromatographic mass spectrometry (Table 3).

Compound III_3 could not be isolated; it was identified chromatographically from the linear dependence of the logarithms of the retention times in the III_1-III_3 series on the number of monomeric links in the molecule and also on the basis of an examination of the mass spectra.

The PMR spectra of III_1 and III_2 contain characteristic multiplet signals of protons of the 1,4-dioxane ring at 3.42-4.64 ppm, as well as signals of protons of methyl (0.83 ppm) and methylene and methylidyne groups (1.11-1.44 ppm, m).

A study of the mass spectra of telomer homologs IIIn (n = 1-3) showed that peaks of ions with a mass of 87 (it is the maximum peak for III_1 and III_2), which are formed in the

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TABLE 1. Balance of the Radical Telomerization of 1-Hexene by 1,4-Dioxane (150°C, 1 h, 0.6 mmole of TBP)

Charge, mmole		Consumed, mmole		Formed, mmole		
1,4-dioxane	1-hexene	1,4-dioxane	1-hexene	III_1	III_2	III_3
11,4	2,4	0,7	0,9	0,5	0,1	0,1
11,3	4,7	1,3	2,1	0,9	0,4	0,2
11,4	5,5	1,5	2,1	0,8	0,3	0,2

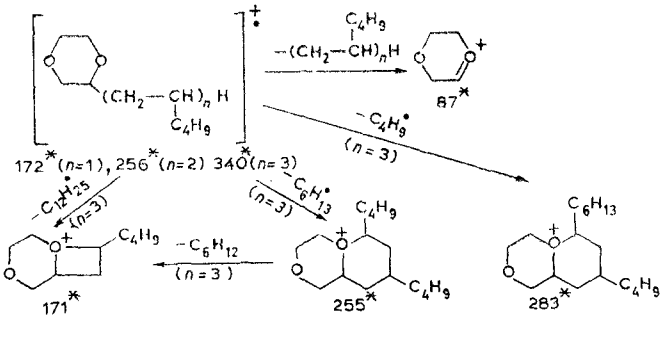
TABLE 2. Partial Chain Propagation Constants in the Radical Telomerization of 1-Hexene (II) by 1,4-Dioxane (I) (150°C, 1 h, [TBP] = 3.2%)

Initial charge, mmole		Conversion			Amounts of telomer homologs III_n, mole				Partial chain-propagation constants C		
I	II	K_{II}*, %	K_I*, %	$\frac{K_{II}}{K_I}$	III_1	III_2	III_3	$III_{n>3}$	C_1	C_2	C_3
11,35	1,21	39	8	0,09	82	12	4	2	0,36	0,19	0,18
11,36	2,38	40	6	0,17	66	21	8	5	0,33	0,26	0,26
11,26	3,50	40	7	0,25	60	17	11	12	0,40	0,20	0,22
11,30	4,71	44	7	0,33	56	18	10	16	0,45	0,24	0,24
11,36	5,47	39	15	0,41	54	18	11	17	0,49	0,27	0,27
Arithmetic-mean values of partial constants C_n									0,41	0,23	0,23
Arithmetic-mean error									0,05	0,03	0,03

TABLE 3. Physicochemical Constants and Mass Spectra of the Reaction Products

Compound	n_D^{20}	d_4^{20}	bp, °C (mm)	Found, %		Empirical formula	Calc., %		Mass spectrum, m/z (relative intensity, %)
				C	H		C	H	
III_1	1,4412	0,918	77—79 (2)	70,16	11,32	$C_{10}H_{20}O_2$	69,70	11,72	43 (33,6), 44 (23,3), 55 (18,2), 57 (14,8), 59 (16,4), 70 (18,0), 87 (100,0), 97 (10,7), 113 (6,3), 172 (8,1)
III_2	1,4529	0,896	120—122 (1)	74,26	12,98	$C_{16}H_{32}O_2$	74,92	12,60	43 (44,7), 45 (21,7), 55 (36,6), 57 (39,1), 59 (29,8), 87 (100,0), 97 (16,2), 137 (15,7), 171 (17,9), 194 (18,7), 256 (1,2)
III_3	—	—	—	—	—	—	—	—	43 (58,1), 45 (6,4), 55 (30,9), 57 (39,5), 59 (32,4), 69 (18,6), 71 (22,0), 73 (17,4), 87 (22,9), 141 (41), 171 (100), 255 (62,3), 283 (6,8)

dissociation of the molecular ion at the exocyclic bond, are characteristic for these compounds. Low-intensity molecular-ion peaks with masses of 172 and 256, respectively, are observed in the mass spectra of telomers III_1 and III_2. The remaining ions are evidently formed as a result of the successive splitting out of hydrocarbon fragments from the molecular ion. On the basis of the data obtained, the following scheme of the fragmentation of III_n under the influence of electron impact can be proposed:



* m/z values.

In addition, peaks of hydrocarbon ions (43, 55, 57, etc.) are intense in the mass spectra of telomer homologs III_n.

EXPERIMENTAL

Telomerization was carried out in thick-walled ampuls by the method described in [5] at 150°C for 1 h.

The mass spectra were obtained with a Finnigan-4021 chromatographic mass spectrometer with a glass capillary column (5 m, SE-30); the ionizing voltage was 70 eV, and the source temperature was 250°C. The PMR spectra of solutions of the compounds in CCl_4 were obtained with a Tesla BS-497 spectrometer (100 MHz) with hexamethyldisiloxane as the external standard. The reaction products were isolated by preparative GLC with a PAKhV-08 chromatograph with a catharometer; the carrier gas was helium, the flow rate was 3.6 liters/h, and the 1200 by 9 mm column was packed with 20% SKTFT-50 on Chromaton N-AW. Quantitative analysis of the reaction products was carried out by the GLC method on the Tsvet-152 device (catharometer, gas carrier was helium at flow rate 3.0 liter/h, column 3000 × 4 mm was packed with 20% SKFT-50 on chromaton N-AW).

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