POLYCONDENSATION OF gem-DIHALOCYCLOPROPANES UNDER THE INFLUENCE OF LITHIUM

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The polymerization of gem-dihalocyclopropanes under the influence of various catalysts, which proceeds with the opening of the three-carbon ring, was studied previously [1-3]. We studied the polycondensation of various gem-dihalocyclopropanes: the 1, 1-dichloro-(I), 1, 1-dichloro-2-n-propyl-(II), 1, 1-dichloro-2-tolyl-(III), and 1, 1-dibromo-2-n-butyl-(IV)-cyclopropanes, and also the 7, 7-dichloro- and 7, 7dibromobicyclo[4.1.0]heptanes, (V) and (VI) respectively. The selection of these study objects is explained by the simplicity of their preparation and by the presence of two halogen atoms in their molecules, the intermolecular cleavage of which assures the formation of macromolecules. We used lithium in THF medium as the dehalogenating agent. According to [4], various polyhalo-substituted hydrocarbons easily form highmolecular compounds under these conditions.

It is known [5] that gem-dihalocyclopropanes react with lithium alkyls to form α -halo lithium compounds [6] as the intermediate products. Under the influence of lithium, monohalocyclopropanes [7, 8] form cyclopropyllithium derivatives. The polycondensation of gem-dihalocyclopropanes under the influence of Li will apparently proceed with a retention of the ring according to the scheme:



An alternate mechanism for progress of the reaction is the intramolecular cleavage of LiX in the intermediate organolithium compound (VII) with the formation of allenes [8, 9]. It is not excluded that the latter is polymerized according to the scheme proposed by us:



As it proved, the reaction of the indicated dihalides with lithium in THF medium at $0-50^{\circ}$ leads to the formation of oligomers, with a mol. wt. of 300-700, in 27-88% yields (Table 1). Reaction is practically absent at a temperature below 0°. The intermolecular cleavage of LiX proves to be more preferable for (V) than for (VI) under the same conditions. The polycondensation product from (I) is a pale yellow powder, while the other oligomers are colored viscous liquids.

The structure of the synthesized oligomers was judged on the basis of the IR and NMR spectra, and also on the basis of the turbidimetric titration data. Together with the lines that are characteristic for a 3-membered ring [10] (1010-1020, 3010-3020, 3100-3110 cm⁻¹), the absorption bands of the C-Cl and C-Br bonds ($600-800 \text{ cm}^{-1}$) are present in the IR spectra of compounds (I)-(VI). The complete (or almost

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complete) disappearance of the absorption bands of the C-Hal bonds is observed in the IR spectra of all of the obtained oligomers, whereas the lines of the cyclopropane ring are retained. Besides this, absorption bands in the 2800-2900 cm⁻¹ region are observed in the spectra of oligomers (VII)-(X) (respectively obtained from (I)-(IV)), which are characteristic for noncyclic methylene groups, and are somewhat more intense than in the spectra of the starting monomers. In the spectra of (VII), (VIII), (XI), and (XII) (respectively obtained from (I), (II), (V), and (VI)) are present weak absorption bands in the 1600-1700 cm⁻¹ region, which characterize the presence of double bonds, whereas these lines are absent in the spectra of (IX) and (X); absorption lines in the 1800-1900 cm⁻¹ region, characteristic for intracyclic double bonds [11], are also not observed in the spectra of the oligomers. As was to be expected, the lines, characteristic for the corresponding R radical, are retained in the spectra of (VIII)-(XII). As a result, from an analysis of the IR spectra of the oligomers it follows that, together with the formation of polycyclopropane structures, a partial opening of the 3-membered rings occurs. In the case of (III)-(VI) the formation of polycyclopropane is the predominant direction of the reaction.

A similar conclusion can be made from an analysis of the NMR spectra. The structure of a polycyclopropane is most distinctly confirmed on the example of oligomer (IX). Multiplets with δ 1.70 and 2.75 ppm, which are characteristic for the starting halo-containing cyclopropane ring, are absent in the spectra of oligomer (IX). Together with the signals of the protons of the CH₃ and C₆H₅ groups (δ 2.3 and 7.0 ppm), new signals appear in the spectrum of (IX), with δ 0.6, 1.2, and 1.4 ppm, which are characteristic for the protons of arylcyclopropanes [12]. The observed changes in the spectra of the monomers and oligomers testify to the progress of dehalogenation and the retention of the 3-membered ring in the reaction products.



Fig. 1. Turbidimetric titration curves of oligomers: 1 and 3) for oligomers obtained from (III); 2 and 4) for oligomers obtained from (IV).

In the spectra of oligomers (VIII), (X), (XI), and (XII) an overlapping of the signals of the protons of the 3-membered ring and the protons of the substituent make it quite difficult to obtain information regarding their structure. Nevertheless, the appearance of a weak signal of olefinic protons (δ 5.6 ppm) in the spectra of (VIII), (XI), and (XII) corroborates a partial opening of the 3-membered ring.

In Fig. 1 are shown the turbidimetric titration curves of the oligomers obtained from (III) and (IV). The smoothness of titration curves 1 and 2, and the absence of inflections, testify to the high degree of uniformity of the products. Differential curves 3 and 4 represent one peak, which also suggests that the oligomers have a uniform composition.

EXPERIMENTAL

The IR spectra were taken on a UR-10 spectrophotometer (the liquids in cells with a thickness of 0.05-5 cm, and the solid products as KBr pellets). The NMR spectra were obtained on a JNM-3H-60 spectrometer in CCl₄ solutions at 20°, using HMDS as the standard.

1, 1-Dichlorocyclopropane (I) was obtained as described in [13], bp 74.5°; n_D^{25} 1.4378. 1, 1-Dichloro-2-n-propylcyclopropane (II) was obtained at 0° from 1-pentene, sodium methylate and ethyl trichloroacetate (ETCA) as described in [14], bp 59° (42 mm); n_D^{20} 1.4488; cf. [15]. 1, 1-Dichloro-2-tolycyclopropane (III) (mixture of isomers) was prepared by the

TABLE 1. Preparation Conditions and Characteristics of Oligomers

Starting gem-dihalo- cyclopropane (DHC)	DHC:THF: Li mole	Reaction conditions		Yield of oligomer.		Found		
	ratio	т.,∘с	time, h	%of theory	M ol. wt	C, %	Н, %	Cl (Br) %
I II III Mixture of o- and p-isomers	$\begin{array}{c} 1:5:5\\ 1:60:5\\ 1:65:5 \end{array}$	5 50 10	25 15 15	50 39 88	390 600 700	76 ,99 74 ,12 83 ,20	10 ,57 9 ,89 7 ,67	1,03 0,0 0,56
IV	1:4:5	40	15	75	400	86.06	12.86	0.0
V	1:4:5	20	15	54	360	84.64	11.02	0.0
VI	1:4:5	-20	15	27	320	82.42	10.70	3.77

dichloromethylenation of vinyltoluene (mixture of o- and p-isomers) as described in either [14] or [16], bp $83-85^{\circ}$ (2 mm); n_{D}^{20} 1.5465; cf. [17]. 1,1-Dibromo-2-n-butylcyclopropane (IV) and 7,7-dihalobicyclo[4.1.0]-heptanes (V) and (VI) were synthesized as described in [18], and had constants that corresponded to the literature data.

Synthesis of Oligomers. To a mixture of the gem-dihalocyclopropane and THF, with the constant passage of dry nitrogen and stirring, was added lithium as thin platelets in portions over 2 h. In the case of marked exothermic heat the flask was cooled in ice water. The oligomer from (I) was reprecipitated from THF solution by pouring into water. The resinlike liquids, obtained from (II)-(VI), were dissolved in ether, the solutions were washed with water until the test for Cl⁻ and HO⁻ was negative, and after removing the solvent the residues were dissolved in THF and reprecipitated by pouring into water. The oligomers were dried at 30° (10 mm) over P_2O_5 to constant weight. The molecular weight of the oligomers was determined by the thermoelectric method from the value of the temperature maximum [19] for their solutions in THF, with the thermostat temperature kept constant with an accuracy of +0.005°.

CONCLUSIONS

1. The polycondensation of a number of gem-dihalocyclopropanes under the influence of lithium in tetrahydrofuran medium gave oligomers with an average mol. wt. of 300-700.

2. An analysis of the IR and NMR spectra testifies to the main retention of the 3-membered ring during the polycondensation process.

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