REACTION OF SPIRO ORTHO ESTERS WITH POLAR REAGENTS

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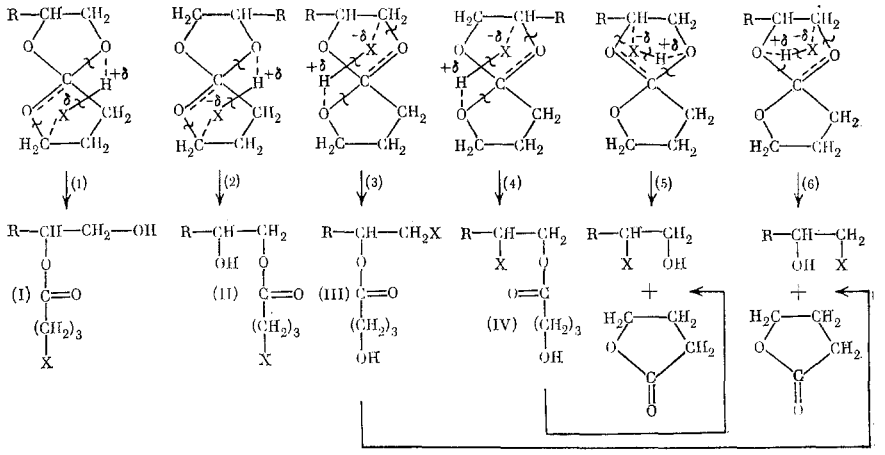
In recent years a new line of research involving the synthesis of monomers capable of polymerizing with zero shrinkage or with an increase in volume, has developed in the chemistry of oxygen-containing rings. Spiro ortho esters (SOEs) [1, 2], bicyclic ortho esters [3], and spiro orthocarbonates [4] have been used for this purpose. From the standpoint of practical use the most promising are the SOEs synthesized from relatively available initial products under mild conditions [5]. In addition, from diepoxides or γ-butyrolactone or its analogs it is possible to synthesize bisspiro ortho esters, from which it is possible to obtain cross-linked polymers with zero shrinkages.

During chain initiation and propagation in cationic polymerization each of the three O atoms in the SOE molecule can undergo attack by the catalyst or by the active center. This leads to opening of the rings in different orders and to the formation of polymers with somewhat different structures. In addition, attack by the monomer on the exocyclic C^2 atom can lead to the elimination of a lactone, which impairs the characteristics of the obtained polymer.

In order to determine the most likely direction of attack by the SOE and the mechanism of ring opening we investigated the reactions of 2-chloromethyl-1,4,6-trioxaspiro[4.4]nonane (CMS) with polar reagents (water, hydrogen chloride, and methanol) without a catalyst and in the presence of boron trifluoride etherate.

Scheme 1



All the possible paths for the reaction of the HX molecules and the SOE are shown in Scheme 1. The addition of HX to the O and C atoms of the various rings leads to the formation of hydroxyesters (HEs) of type (I-IV). If one of the O atoms of the dioxolane ring undergoes initial attack, the X^- fragment adds to the tetrahydrofuran ring, and the HEs of type (I) or (II) is formed; if initial attack occurs at the tetrahydrofuran ring, the HE (III) or (IV) is formed. The products from the addition of the HX molecule to the O and C atoms of one dioxolane ring must be γ-butyrolactone and the alcohol.

Investigation of the composition during the reaction showed that in all cases with short conversion times only the hydroxy esters are formed and their concentrations pass

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TABLE 1. Composition of the Products from the Reaction of CMS with Water in Methylene Chloride without a Catalyst

Time, min	c_{CMS}	c_{est}	c_{lac}	Σc
	×10, M			
0	6,90	0	0	6,90
22	4,35	2,08	0,14	6,57
49	4,05	2,42	0,19	6,66
142	0	4,68	0,52	5,20
174	0	5,38	0,56	5,94
2805	0	6,03	0,82	6,85
8600	0	3,22	3,80	7,02

TABLE 2. Composition of the Products from the Reaction of CMS with Water in the Mass without a Catalyst

Time, min	c_{CMS}	c_{est}	c_{lac}	Σc
	×10, M			
0	3,02	0	0	3,02
106	1,43	2,37	0,05	3,85
1217	0	3,38	0,09	3,47
7034	0	0,88	2,41	3,29
12 630	0	0,06	2,72	2,78

TABLE 3. Composition of the Products from the Reaction of CMS with Methanol in Methylene Chloride Solution in the Presence of Boron Trifluoride Etherate $[BF_3 \cdot Et_2O] = 5 \cdot 10^{-2}$ M

Time, min	c_{CMS}	c_{est}	c_{lac}	Σc
	×10, M			
0	3,06	0	0	3,06
4	3,06	0,11	0	3,17
32	2,67	0,35	0,06	3,08
66	2,52	0,44	0,14	3,10
3814	0,84	2,40	0,30	3,54

TABLE 4. Composition of the Products from the Reaction of CMS with Hydrogen Chloride in Methylene Chloride Solution without a Catalyst

Time, min	c_{CMS}	c_{est}	c_{lac}	Σc
	×10, M			
0	3,51	0	0	3,51
23	1,09	2,26	0,05	3,40
164	0	3,44	0,54	3,98
1074	0	3,33	0,48	3,81

through a maximum (Tables 1-4). As the hydroxy ester is used up, the lactone accumulates in the system. Typical curves for the consumption of CMS, the accumulation and consumption of the hydroxy esters, and the accumulation of the lactone are given in Fig. 1. In all cases the CMS is fully consumed. With the CMS and water in an equimolar ratio the reaction ends with the disappearance of the hydroxy ester. The maximum concentration of the lactone is

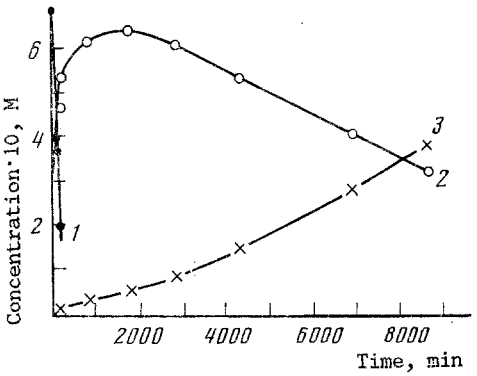


Fig. 1. The kinetic relationships for the reaction of CMS with water without a catalyst in methylene chloride at 20°C: 1) CMS; 2) ester; 3) γ-butyrolactone. $[CMS]_0 = [H_2O]_0 = 0.69$ M.

almost equal to the initial concentration of the CMS (Table 2).

The CMS does not react with methanol without a catalyst; in the presence of boron trifluoride etherate the reaction takes place more slowly than the reaction of CMS with water or hydrogen chloride in the absence of a catalyst (Tables 1-4).

The overall concentration of the hydroxy ester and the lactone during the reaction is equal to the concentration of consumed CMS (Tables 1-4), and the reaction mixture does not contain any unidentified products. This makes it possible to rule out a different reaction path.

The results show that the reaction of CMS with polar reagents takes place through the formation of the hydroxy esters (I-IV). The low concentration of the lactone at the beginning of the reaction (Tables 1-4, Fig. 1) makes it possible largely to exclude the path leading to the direct formation of the lactone from the CMS. The lactone is formed as a result of the monomolecular cleavage of the hydroxy ester into the lactone and the glycol or alcohol. If X = OH, reactions (I-IV) lead to the formation of hydroxy esters of types (III) and (IV) and then to the lactone. This is confirmed experimentally by the total conversion of the CMS into the lactone and the glycol. If X = OCH_3 or Cl, the hydroxy esters of types (I) or (II) are not capable of eliminating the lactone. Consequently, the final ratio of the concentrations of the hydroxy ester and the lactone reflects the contributions from reactions (I) and (2) and reactions (3) and (4) to the mechanism for the reaction of CMS with polar reagents. As seen from the data in Table 4, this ratio is ∿7:1. This indicates a significant difference between the reactivities of the oxygen atoms in the dioxolane and tetrahydrofuran rings.

Thus, the reaction of the spiro ortho ester with polar reagents takes place with preferential protonation of the oxygen atom in the dioxolane ring; the addition of HX to the dioxolane ring alone can be ruled out.

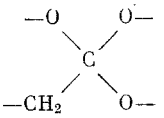
The absence of the addition of HX to the dioxolane ring along corresponds to the rules of stereoelectronic control, according to which an equatorial group is never eliminated directly [6], i.e., hydrolysis must lead only to the hydroxy ester. These results are confirmed by published data [7], where it was shown that ortho esters based on γ-butyrolactone and γ-valerolactone are hydrolyzed to hydroxy esters but not to lactones. The formation of the lactone during the storage of the spiro ortho ester is evidently due to the reaction of the SOE with the impurities and moisture through the intermediate hydroxy esters. Since general relationships are observed in the reaction of CMS with polar reagents in the presence of boron trifluoride etherate and without a catalyst, it can be supposed that the mechanism of ring opening in the polymerization process is similar to the mechanism of the reaction of the spiro ortho ester with polar reagents.

EXPERIMENTAL

The 2-chloromethyl-1,4,6-trioxaspiro[4.4]nonane (CMS), which was obtained by the method in [5], was distilled twice under vacuum [bp 104°C (13 mm Hg)] and was stored in sealed tubes

in an atmosphere of argon. The boron trifluoride etherate was dried over phosphorus pentoxide and distilled under vacuum over fresh portions of phosphorus pentoxide; bp 66°C (25 mm Hg). The methylene chloride was dried and distilled over phosphorus pentoxide. The methanol was purified with calcium hydride and distilled.

The reactions of CMS with water, methanol, and hydrogen chloride were realized at ∿20°C in the mass and in methylene chloride solution. The catalyst was added after the reagents had been mixed in an equimolar ratio.

Gaseous hydrogen chloride was passed through the solution of CMS in methylene chloride until the CMS was completely consumed. The consumption of the CMS was monitored from the change in the optical density of the absorption band at 1327 cm^{-1}, which was assigned to the deformation vibrations of the  group in the spiran ring. The analogous absorption band in the IR spectra of 2-methylene-1,4,6-trioxaspiro[4.4]nonane [8] was assigned to the vibrations of the CH_2 group in the spiro rings. The reaction products were monitored from the appearance of absorption bands at 1730 cm^{-1} (the stretching vibrations of the ester C=O groups), 3557 cm^{-1} (the stretching vibrations of the nonbonded OH group), and 1780 cm^{-1} (the stretching vibrations of the lactone C=O group) in the IR spectra. On account of the mutual overlap of the absorption bands for the ester and lactone C=O groups the optical density of each band was calculated separately [9].

The products from the reaction of CMS with gaseous hydrogen chloride were submitted to fractional distillation at atmospheric pressure in a stream of argon, and the fractions boiling at 198–202 and 204–208°C were collected.

CONCLUSIONS

1. The reaction of 2-chloromethyl-1,4,6-trioxaspiro[4.4]nonane with polar reagents, which models the cationic polymerization of spiro ortho esters, takes place with preferred protonation of one of the oxygen atoms of the dioxolane ring and subsequent addition of the counterion to the α-carbon atom of the tetrahydrofuran ring.

2. The accumulation of the lactone during the storage of the spiro ortho esters is due to reactions with polar impurities, where the intermediate products are hydroxy esters.

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