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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Acid-Catalyzed Condensation of Vinyl-*gem*-dichlorocyclopropanes with Formaldehyde in Nonaqueous Solutions

S. V. Kopsov and S. S. Zlotskii

Ufa State Petroleum Technical University, Ufa, Bashkortostan, Russia

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Abstract—Condensation of vinyl- and vinylmethyl-1,1-dichlorocyclopropanes with formaldehyde in organic solvents of various polarities was studied.

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Reaction of olefins with formaldehyde in the presence of acid catalysts (Prins reaction) is the main route to substituted 1,3-dioxanes [1–4]. This process is widely used in commercial synthesis of 4,4-dimethyl-1,3-dioxane whose cleavage yields isoprene [3]. The condensation is performed most frequently in an aqueous solution, but in this case it is accompanied by formation of hydroxyl-containing by-products: unsaturated alcohols, diols, hydroxyfurans, etc. [4].

To prepare dioxanes containing a *gem*-dichlorocyclopropane fragment, which can be of interest as biologically active compounds and intermediates for organic synthesis, we used the reaction of vinyl-*gem*-dichlorocyclopropanes **Ia** and **Ib** with formaldehyde in organic solvents (1,2-dichloroethane, chlorobenzene, 1,4-dioxane, diisopropyl ether) in the presence of catalytic amounds of H_2SO_4. The starting vinyl-*gem*-dichlorocyclopropanes are formed in virtually quantitative yield by the addition of dichlorocarbene to the corresponding dienes in a two-phase system [5].

We found that the reaction of **Ia** and **Ib** with formaldehyde yielded the coresponding 1,3-dioxanes (**IIa**, **IIb**) and 1,3-dioxolanes (**IIIa**, **IIIb**) in comparable amounts. Apparently, the highly reactive intermediate unsaturated alcohol reacts with formaldehyde to form a hemiacetal whose hydroxy group undergoes intramolecular adition to the double bond to form heterocycles **IIa**, **IIb**, **IIIa**, and **IIIb**:

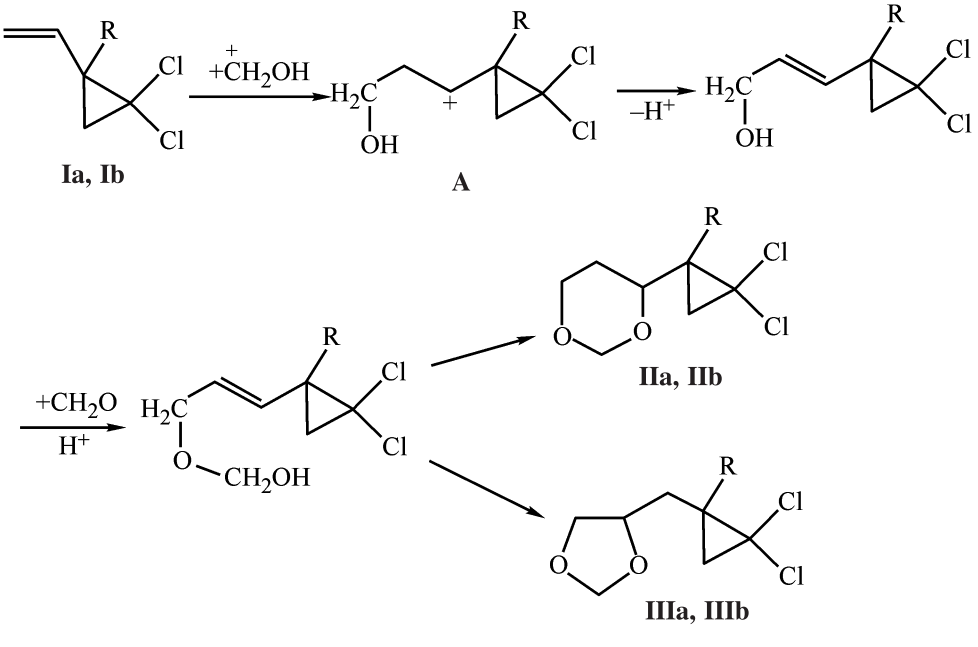


Table 1. Reaction of vinyl-*gem*-dichlorocyclopropanes **Ia** and **Ib** with formaldehyde. Molar ratio of **Ia** or **Ib** to CH_2O and H_2SO_4 1 : 2.5 : 0.5, 55°C, 3 h

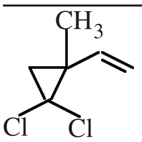
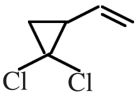
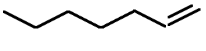
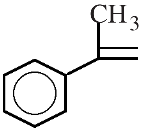
Solvent	Conversion, %		Selectivity, %			
	Ia	**Ib**	**Ia**	**Ib**	**Ia**	**Ib**
1,2-Dichloroethane	95	85*	40	50	35	35
Chlorobenzene	65	60	45	45	45	40
1,4-Dioxane	50	40**	70	50	40	20
Diisopropyl ether	95	90	75	60	35	20

* More than 20% high-boiling unidentified products.
** About 5% low-boiling components.

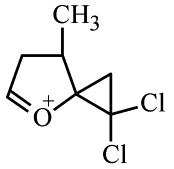
where R = H (**a**), CH_3 (**b**).

It is interesting that, in polar solvents (1,4-dioxane, diisopropyl ether), the selectivity with respect to 1,3-dioxanes **IIa** and **IIb** is somewhat higher than in chlorinated hydrocarbons (Table 1). Apparently, the ratio of the six- (**IIa**, **IIb**) and five-membered (**IIIa**, **IIIb**) products is determined by the rate of proton addition to carbon atoms of the double bond of the intermediate hemiacetal. In the isoprene derivative, the methyl group facilitates the formation of carbocations in which the positive charge is conjugated with the quasiaromatic orbitals of the three-membered carbocycle, which may be responsible for the observed prevalence the reaction pathway leading to the six-membered heterocycle.

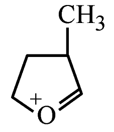
Table 2. Relative activity of olefins in the Prins reaction. Olefin : CH_2O : H_2SO_4 molar ratio 1 : 2.5 : 0.5, 55°C, 30 min, solvent $(i\text{-}Pr)_2O$

Compound	Relative activity
	1
	2.5
	0.5
	15

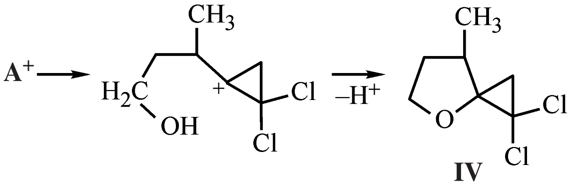
The reaction with **Ia** in 1,2-dichloroethane yields more than 20% high-boiling unidentified products, which may be due to hindered cyclization of oligoformals and formation of noticeable amounts of polyformals. The condensation with **Ia** in 1,4-dioxane yields an impurity of low-boiling substances. The mass spectrum of one of them contains peaks of ions **B** and **C** with *m*/*z* 179 and 85, respectively. We believe that this minor component (1–1.5%) is spirocyclic compound **IV** formed by 1,2-migration of the methyl group and closure of the pyran ring in intermediate carbocation **A**:



B, *m*/*z* = 179



C, *m*/*z* = 85



IV

Sigmatropic shifts in the course of the Prins reaction were observed previously [6].

The activity of olefins **Ia** and **Ib** was compared with that of 1-heptene and styrene in competitive reactions. The relative activity of these unsaturated compounds was judged from the rates of formation of 1,3-dioxacyclanes **IIa**, **IIb**, **IIIa**, and **IIIb** and of 4-amyl- and 4-methyl-4-phenyl-1,3-dioxanes which are selectively formed from 1-heptene and α-methylstyrene, respectively [1]. The activity of the aromatic olefin exceeds that of **Ia** by more than an order of magnitude, and compound **IIa**, in turn, is two times more active than the terminal linear unsaturated hydrocarbon (Table 2).

Table 3. Constants and spectral characteristics of the products obtained

Compound	T_b, °C/P, mm Hg	R_f	^{1}H NMR spectrum, δ, ppm	Mass spectrum, m/z (I_{rel}, %)
4-(2,2-Dichlorocyclopropyl)-1,3-dioxane **IIa**	111/5	0.35	1.4–1.5 (m, 1H, $CHCCl_2$); 1.6–1.8 (m, 2H, CH_2CCl_2); 1.85–2.1 (m, 2H, CH_2); 3.6–3.8 (m, 2H, CH_2O); 4.0–4.15 (m, 1H, CHO); 4.6–5.0 (d.d, 2H, OCH_2O)	198, 200 (0.7) [M^+]; 109, 111 (5); 87 (100); 57 (60)
4-(2,2-Dichloro-1-methylcyclopropyl)-1,3-dioxane **IIb**	115/5	0.37	1.35 (s, 3H, CH_3); 1.4–1.6 (d.d, 2H, CH_2CCl_2); 2.4–2.6 (m, 2H, CH_2); 3.6–3.8 (m, 2H, CH_2O); 3.95–4.15 (m, 1H, CHO); 4.65–5.0 (d.d, 2H, OCH_2O)	212, 214 (1) [M^+]; 123, 125 (3); 87 (100); 57 (51); 45 (81)
4-(2,2-Dichlorocyclopropylmethyl)-1,3-dioxolane **IIIa**	105/5	0.27	1.4–1.5 (m, 1H, $CHCCl_2$); 1.6–1.8 (m, 2H, CH_2CCl_2); 1.6–2.1 (m, 2H, CH_2); 3.5–3.8 (m, 2H, CH_2O); 4.1–4.25 (m, 1H, CHO); 4.6–5.0 (d.d, 2H, OCH_2O)	198, 200 (0.1) [M^+]; 100 (45); 84 (50); 73 (100)
4-(2,2-Dichloro-1-methylcyclopropylmethyl)-1,3-dioxolane **IIIb**	108/5	0.30	1.4 (s, 3H, CH_3); 1.4–1.6 (d.d, 2H, CH_2CCl_2); 1.6–2.2 (m, 2H, CH_2); 3.4–3.7 (m, 2H, CH_2O); 4.05–4.2 (m, 1H, CHO); 4.6–5.1 (d.d, 2H, OCH_2O)	212, 214 (0.1) [M^+]; 114 (37); 84 (40); 73 (100)

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz) in acetone-d_6, $CDCl_3$, or C_6D_6 + CCl_4. GLC analyses were performed on a Tsvet-500M device (flame ionization detector, 5 × 1000-mm metal column, stationary phase 5% SE-30 on Chromaton N-AW, programmed heating from 50 to 220°C at a rate of 6 deg min^{-1}, carrier gas helium).

Vinyl-*gem*-dichlorocyclopropanes **Ia** and **Ib** were prepared by the published procedure [5]. The unsaturated compounds used in the study were no less than 99% pure.

Acid-catalyzed reaction of olefins with formaldehyde (general procedure). A solution of 0.1 mol of appropriate olefin in 10 ml of appropriate solvent was added with vigorous stirring to a mixture of 7.7 g (0.26 mol) of paraform, 3.1 ml of concentrated H_2SO_4, and 5 ml of the solvent. The mixture was heated to 50–60°C, with the stirring continued, until the paraform dissolved completely. After cooling, the mixture was neutralized with aqueous ammonia, the organic layer was separated and dried over $CaCl_2$, and the solvent was evaporated. The products were isolated by column chromatography on silica gel (eluent hexane–ethyl acetate, 6 : 1).

Some characteristics of the synthesized compounds are given in Table 3.

CONCLUSION

Condensation of vinyl- and vinylmethyl-*gem*-dichlorocyclopropanes with formaldehyde in organic solvents of various polarities was performed. The reaction occurs along two parallel pathways, yielding the corresponding 4-*gem*-dichlorocyclopropyl-1,3-dioxolanes and -1,3-dioxanes via the intermediate unsaturated alcohol.

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