INVESTIGATIONS ON REACTIONS OF CYCLENE α-OXIDES

II. Influence of the Reaction Conditions on the Order of Addition of Alcohols and α-Chloro Ethers to Dioxides of 1-Vinyl-3-cyclohexene in an Acid Medium*

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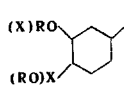
The influence of the reaction conditions on the order of addition of alcohols and α-chloro ethers in an acid medium to dioxides of 1-vinyl-3-cyclohexene is described on the basis of a determination of the percentage content of the ratio of the isomers by IR spectroscopy. It has been established that under mild conditions the addition takes place selectively with the predominant opening of the oxide ring attached to the six-membered carbon ring. More severe conditions (higher temperature, smaller amount of solvent) favor the formation of isomers with an opened oxide ring on the ethylene grouping.

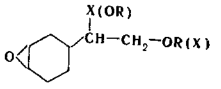
We have previously shown on the basis of a quantitative study of IR absorption spectra that the addition of acid and basic reagents to the dioxide of 1-vinyl-3-cyclohexene takes place with the opening of the oxide ring attached to the six-membered carbon ring or with the opening of the oxide ring of the ethylene grouping of the dioxide [1,2].

In an acid medium, alcohols, chloro ethers, and dialkyl phosphorochloridites add predominantly to the epoxycyclohexane group, and basic reagents such as, for example, alcohols in the presence of sodium, and amines react with the oxide ring of the ethylene grouping [1,2].

In a more detailed study of these reactions in an acid medium, it was found that the reaction conditions (temperature, amount of solvent) have a great influence on the selectivity of addition; depending on them, the product of addition to the oxide ring of the ethylene grouping (II) may be formed to a greater or smaller extent, in addition to the product of addition to the oxide ring attached to the six-membered carbon ring (I).



I



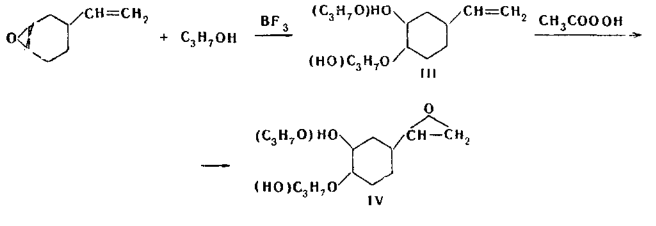
II

$X = OH$, $R = -C_3H_7$,
$X = Cl$, $R = -CH_2OCH_3$, $-CH_2OC_2H_5$, $-CH_2OC_3H_7$

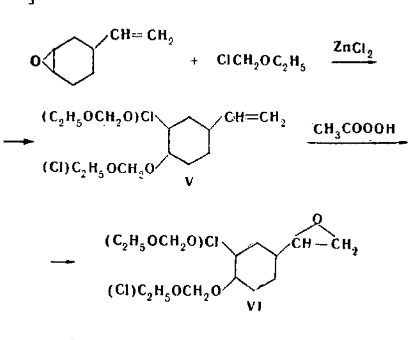
In the present communication, we give the results of a more detailed study of the reaction of 1-vinyl-3-hexene dioxide with propanol in the presence of boron trifluoride etherate and with α-chloro ethers in the presence of zinc chloride.

In studying the reaction with propanol, our attention was directed to the fact that reaction products with different constants were obtained, depending on the temperature of the reaction mixture and on the amount of solvent (the same alcohol) (Table 1). With an increase in the temperature of the reaction mixture or with a decrease in the amount of solvent, the refractive index and the specific gravity increased, which shows a change in the ratio of the isomers in the reaction products.

In order to determine the percentage content of isomers with an unopened epoxyethyl ring in the reaction product, measurements were made of the peak intensities of the characteristic absorption bands $\nu as CH_2$ (3050 cm^{-1}) of the epoxyethyl grouping [3]. The measurements were carried out in an IKS-14 infrared spectrometer with an LiF prism by the double-beam scheme. Potassium bromide cells with a single layer thickness (0.062 cm) were used for all the samples. The concentrations of the solutions (in CCl_4) were selected in such a way that the optical densities ($\log I_0/I$ were between 0.20 and 0.60. The measurements were carried out by the base line method [4], the tangent to the background at the point $\nu \approx 3200$ cm^{-1} being selected as the base line. The correctness of this selection was confirmed by studying the fulfillment of the Lambert-Beer law for solutions of standard substances. The errors introduced by neglecting the absorption of the second component (II) at the point of measurement did not exceed 10%. For a number of products, the isomer content was also determined from a calibration graph constructed with standard mixtures. The difference between the results of the two methods was not greater than 10%. To determine the absorption coefficient k_{3050}, the standard compounds IV [1-epoxyethyl-3(4)-hydroxy-4(3)-propoxycyclohexane]



and VI [1-epoxyethyl-3(4)-chloro-4(3)-ethoxymethoxycyclohexane]



were prepared by independent synthesis.

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*For part I, see [2].

Table 1

Products of the Reaction of 1-Vinyl-3-cyclohexene Dioxide with Propanol

Expt. No.	Reaction conditions			Bp, °C (pressure,mm)	d_4^{20}	n_D^{20}	Yield of addition products, %		Ratio of the isomers I and II in the addition products for 1 mole of alcohol	Analysis of the products of the addition of 1 mole of alcohol*		
	maximum temperature of heating, °C	molar ratio of dioxide to alcohol	time of standing at room temperature, hr				1 mole alcohol	2 moles alcohol		C, %	H, %	MR_D
1	20	1 : 14	1	92.5— 93 (0.035)	1.0524	1.4739	46.0	0	85 : 15	65.79; 65.94	10.07; 10.48	53.50
2	30	1 : 14	3	91.5— 93 (0.025)	1.0524	1.4749	38.5	14.0	70 : 30	66.15; 66.09	10.12; 10.08	53.59
3	40	1 : 14	3	123 —124.5 (3)	1.0538	1.4750	46.0	11.6	65 : 35	65.94; 66.03	9.94; 9.82	53.50
4	35	1 : 12	3	92 — 94 (0.03)	1.0578	1.4761	29.9	17.9	55 : 45	65.79; 65.87	10.19; 10.08	53.39
5	30	1 : 7	3	94 — 95 (0.04)	1.0589	1.4770	22.7	48.9	45 : 55	66.08; 65.81	10.29; 10.17	53.43

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*Calculated for $C_{11}H_{20}O_3$, %: C 65.97; H 10.07; MR_D 53.41.

Table 2

Products of the Reaction of 1-Vinyl-3-cyclohexene Dioxide with 1 Mole of Various α-Chloro Ethers

Expt. No.	Chloro ether added	Reaction conditions			Bp, °C (pressure,mm)	d_4^{20}	n_D^{20}	ratio of isomers I and II	Found			Yield, %
		molar ratio of dioxide and chloro ether	maximum temperature of heating, °C	time of heating, min					C, %	H, %	MR_D	
1	$ClCH_2OCH_3$	1 : 1.5	34	165	89 — 90 (0.01)	1.1704	1.4828	95 : 5	54.68; 54.58	7.72; 7.73	53.83	30.6*
2	$ClCH_2OC_2H_5$	1 : 1.5	60	60	93.5— 95 (0.01)	1.1330	1.4749	90 : 10	56.51; 56.37	8.11; 8.19	58.46	50.4**
3	$ClCH_2OC_2H_5$	1 : 1.7	85	105	94.5— 96 (0.01)	1.1379	1.4770	70 : 30	56.46; 56.53	8.09; 8.04	58.28	22.2**
4	$ClCH_2OC_3H_7$	1 : 1.7	45	90	103 —104.5 (0.01)	1.1092	1.4748	85 : 15	57.88; 57.77	8.69; 8.59	63.17	33.3***
5	$ClCH_2OC_3H_7$	1 : 1.5	65	60	103.5—104.5 (0.01)	1.1121	1.4749	75 : 25	57.80; 57.69	8.62; 8.73	62.99	34.3***
6	$ClCH_2OC_3H_7$	$ZnCl_2$ was added to the chloro ether and then the dioxide was added in drops at 3°-10°C. The mixture was heated at 45°-50°C for 90 min.			103 —105 (0.01)	1.1241	1.4803	35 : 65	57.94; 57.81	8.38; 8.29	62.94	12.2***

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*Calculated for $C_{10}H_{17}ClO_3$, %: C 54.42; H 7.76.

**Calculated for $C_{11}H_{19}ClO_3$, %: C 56.28; H 8.16.

***Calculated for $C_{12}H_{21}ClO_3$, %: C 57.94; H 8.51.

The IR spectra of the model compounds obtained are given in the figure. As follows from the figures of Table 1, under mild reaction conditions with propanol (Experiment 1), the content of isomers with an epoxyethyl group (I) in the reaction products was a maximum. As the temperature was raised to 30°–40° C (Experiments 2 and 3), with the same ratios of the reactants, the content of these isomers gradually decreased and, correspondingly, the content of isomers with an epoxy ring attached to the six-membered carbon ring (II) gradually increased. When the dilution of the reaction mixture with alcohol was decreased (Experiments 4 and 5), approximately equal amounts of I and II were formed. In the first experiment, no product of the addition of 2 moles of alcohol to the dioxide was isolated at all, in the last experiment its yield amounted to 48.9% of theoretical; the constants have been given previously [1].

Similar observations were made with respect to the reaction of 1-vinyl-3-cyclohexene with α-chloro ethers. When the reaction with chlorodimethyl ether was performed in diethyl ether solution, the addition took place almost completely (95%) with the opening of the oxide ring attached to the six-membered carbon ring. In the absence of a solvent (with chloromethyl ethyl and with chloromethyl propyl ethers), the reaction took place very vigorously, making it necessary to apply cooling with a cooling mixture containing solid carbon dioxide. Consequently, the reproducibility of the experiments was somewhat lower than in the reaction with alcohols. When the temperature of the reaction mixture was lowered, the percentage of isomers I in the mixture of products increased. The order of addition was also apparently affected by the manner in which the reaction was performed: whether the zinc chloride was added to a mixture of the reactants or the dioxide was gradually added dropwise to the cooled chloro ether containing the zinc chloride. In the latter case, much resin was formed, it was not always possible to isolate the reaction product, and the ratio of the isomers varied markedly (Table 2).

We found no influence whatever of the reaction conditions on the composition of the products of the interaction of the dioxide with diethyl phosphorochloridite. Regardless of the temperature conditions, the same product with the constants reported previously [2] was isolated. In this case the content of isomers with an epoxyethyl group was 100%.

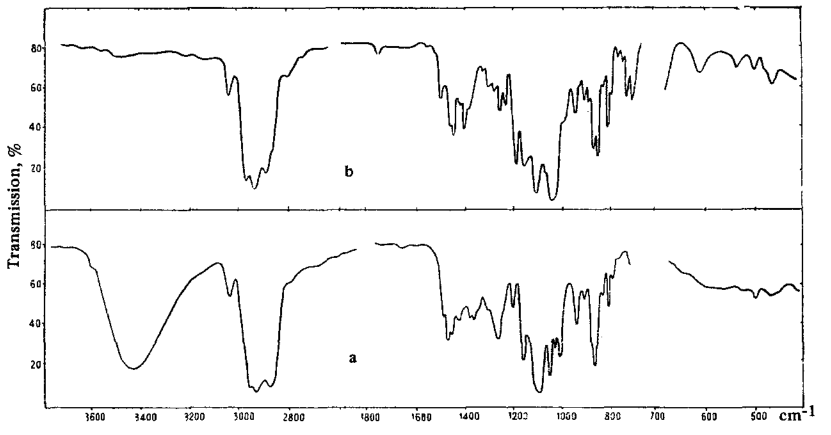
EXPERIMENTAL

Reaction of vinylcyclohexene dioxide with n-propanol. The 1-vinyl-3-cyclohexene dioxide, which was obtained by a method described previously [1], had the following constants: bp 97°–99° C (9 mm); d_4^{20} 1.0967; n_D^{20} 1.4782. Boron trifluoride ethereate was added in drops in an amount of 0.07 ml per 0.1 mole of dioxide to a mixture of the dioxide and n-propanol in the molar ratios shown in Table 1. After some time, the temperature of the reaction mixture rose. It was not allowed to rise above the figure given (ice-water cooling). After cooling, the reaction mixture was kept at room temperature and was then treated with 3% sodium carbonate solution and extracted with ether. The ethereal layer was washed with water and dried with magnesium sulfate. After the ether had been distilled off, the reaction product was twice distilled in vacuum. For constants and analysis, see Table 1.

Synthesis of 1-ethoxyethyl-3(4)-hydroxy-4(3)-propoxycyclohexane (IV).

a) Reaction of the monooxide of 1-vinyl-3-cyclohexene with propanol. The monooxide was obtained by the method given previously [1] and had bp 43.5°–44.5° C (7 mm); d_4^{20} 0.9574; n_D^{20} 1.4684. 0.15 ml of BF_3 etherate was added to a mixture of 30 g (0.242 mole) of the oxide and 145 g (2.413 mole) of propanol (rise in temperature). By cooling, the temperature of the mixture was not allowed to exceed 35° C. After 3-hr standing at room temperature, the reaction mixture was diluted with water and extracted with ether, and the ethereal layer was treated with 3% sodium carbonate solution washed with water, and dried with magnesium sulfate. Two distillations from an Arbuzov flask yielded 30.0 g (67.4%) of 1-vinyl-3(4)-hydroxy-4(3)-propoxycyclohexane (III): bp 113°–114° C (10 mm); d_4^{20} 0.9593; n_D^{20} 1.4691. Found, %: C 71.55; 71.76; H 11.19; 11.00; MR_D 53.52. Calculated for $C_{11}H_{20}O_2$, %: C 71.69; H 10.97; MR_D 53.50.

b) Oxidation of 1-vinyl-3(4)-hydroxy-4(3)-propoxycyclohexane with acetyl hydroperoxide. 16.1 ml of 82.7% acetyl hydroperoxide obtained by B. A. Arbuzov's method [6] was added to 25 g (0.136 mole) of III dissolved in 68 ml of absolute ether. After 8 days' standing at room temperature, the reaction mixture was treated with 7% potassium hydroxide solution and was washed with water, and dried with magnesium sulfate. After the ether had been distilled off, the product was twice distilled in vacuum. This gave 18.0 g (66.2%) of 1-epoxyethyl-3(4)-hydroxy-4(3)-propoxycyclohexane (IV); bp 97°–98° C (0.04 mm); d_4^{20} 1.0478; n_D^{20} 1.4730. Found, %: C 65.77; 65.64; H 10.00; 10.28; MR_D 53.62. Calculated for $C_{11}H_{20}O_3$, %: C 65.97; H 10.07; MR_D 53.41.



IR spectra: a) 1-epoxyethyl-3(4)-hydroxy-4(3)-propoxycyclohexane (IV); b) 1-epoxyethyl-3(4)-chloro-4(3)-ethoxymethoxycyclohexane (VI).

Reaction of vinylcyclohexene dioxide with α-chloro ethers. Zinc chloride at the rate of 0.1 g per 0.1 mole of dioxide was added to a mixture of the dioxide and the chloro ether cooled to +5° C (the ratio of the reactants is shown in Table 2). The temperature of the reaction mixture tended to rise but was kept down to the figure given by cooling. Then the mixture was heated at 40°–45° C for 1–2 hr (about 3 hr in the experiment with chloro dimethyl ether). After the zinc chloride had been filtered off and the excess of chloro ether had been removed under reduced pressure, the residue was distilled twice in vacuum. The reaction in ether was carried out in the same way as in the absence of a solvent except for the fact that the mixture of reactants was dissolved in ether in the proportion of 40 ml of ether to 10 g of dioxide. The yields and constants of the products are given in Table 2.

Synthesis of 3(4)-chloro-1-epoxyethyl-4(3)-ethoxymethoxycyclohexane (VI).

a) Reaction of 1-vinyl-3-cyclohexene monooxide with chloromethyl ethyl ether. At a temperature of 5°–10° C, 20 g (0.211 mole) of the choro ether was added to a solution of 28 g (0.225 mole) of vinylcyclohexene oxide in 40 ml of absolute toluene containing 0.1 g of zinc chloride. Then the mixture was heated for 1 hr 20 min at 40°–45° C, after which the zinc chloride was filtered off and the toluene was distilled off in vacuum. Two distillations of the residue yielded 18.2 g (39.0%) of 3(4)-chloro-4(3)-ethoxymethoxy-1-vinylcyclohexane (V): bp 67°–68° C (0.05 mm); d_4^{20} 1.0342; n_D^{20} 1.4688. Found, %: C 60.76; 60.64; H 8.75; 8.80; MR_D 58.89. Calculated for $C_{11}H_{19}ClO_2$%: C 60.40; H 8.76; MR_D 58.48.

b) Oxidation of 3(4)-chloro-4(3)-ethoxymethoxy-1-vinylcyclohexane with acetyl hydroperoxide. To 13.2 g (0.060 mole) of V dissolved in 30 ml of absolute ether was added 7.2 ml of 82.6% acetyl hydroperoxide. After it had been allowed to stand for 7 days at room temperature, the mixture was treated as described above. After the ether had been driven off, the product was distilled twice in vacuum. This gave 6.8 g (47.9%) of 3(4)-chloro-1-epoxyethyl-4(3)-ethoxymethoxycyclohexane (VI): bp 95°–96° C (0.01 mm); d_4^{20} 1.1283; N_D^{20} 1.4740. Found, %: C 56.31; 56.18; H 8.30; 8.15; MR_D 58.48. Calculated for $C_{11}H_{19}ClO_3$, %: C 56.28; H 8.16; MR_D 58.39.

The elementary analyses were performed by T. S. Krivovaya.

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