

INVESTIGATIONS ON REACTIONS OF CYCLENE α -OXIDES

III. Reaction of 1-Vinyl-3-cyclohexene with Sodioacetoacetic Ester and Halogen Hydrides*

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The reaction of 1-vinyl-3-cyclohexene dioxide with sodioacetoacetic ester and hydrogen halides (HCl, HBr) is described. On the basis of IR absorption spectra, it has been established that the addition of acetoacetic ester takes place to the oxide ring of the vinyl group with the formation of 1-acetyl-2(3)-(3',4'-epoxycyclohexyl)butyrolactone. The addition of HCl depends on the reaction conditions; under mild conditions addition takes place predominantly at the epoxycyclohexane group (85%), and under more severe conditions a mixture of products of addition both to the oxide ring attached to the six-membered carbon ring and to the oxide ring of the ethylene grouping is formed in a ratio of 55 : 45. The ratio of the isomers with epoxyethyl and epoxycyclohexane groups in the product of the addition of HBr is 60 : 40.

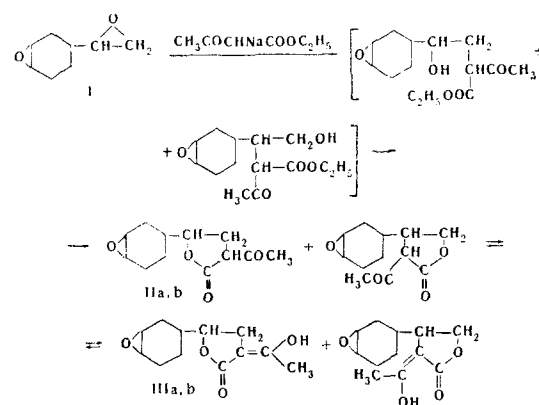
In preceding communications [1-3] it has been shown that the oxide rings of 1-vinyl-3-cyclohexene dioxide react differently according to the medium. In the present communication we give the results of a study of the reaction of 1-vinyl-3-cyclohexene dioxide (I) with sodioacetoacetic ester and with hydrogen halides.

It is known from the literature that sodioacetoacetic ester readily reacts with α -oxides to form the corresponding acetylbutyrolactone derivatives [4, 5]. The IR spectrum of the dioxide is characterized by the presence of the peaks ν_{asCH_2} 3050, 1260, and 870 cm^{-1} of the pulsation and asymmetric vibrations of a monosubstituted epoxy ring. An absorption maximum of medium intensity with $\nu = 920 \text{ cm}^{-1}$ corresponds to the epoxy group condensed with the six-membered ring. From changes in these characteristics it is possible to estimate the order of addition to one or other ring of 1-vinyl-3-cyclohexene dioxide [3].

The IR spectrum of the product of the addition of acetoacetic ester to the dioxide I lacks the peak $\nu_{\text{asCH}_2} = 3050 \text{ cm}^{-1}$ which is the most reliable indication of a terminal epoxy ring, since this region is free from the superposition of other peaks. At the same time, the spectrogram (figure) has a strong peak with $\nu_{\text{C=O}} = 1770 \text{ cm}^{-1}$, which is characteristic for a five-membered lactone ring [6] and absorption bands of a hydroxyl with $\nu_{\text{OH}} = 3500 \text{ cm}^{-1}$ and of a double bond with $\nu_{\text{C=C}} = 1657 \text{ cm}^{-1}$. In addition to $\nu_{\text{C=O}} = 1770 \text{ cm}^{-1}$ the peak of the absorption of the stretching vibrations of the carbonyl group with a frequency of 1722 cm^{-1} is clearly seen.

The reaction product gives a violet coloration with ferric chloride, decolorizes potassium permanganate solution, and forms a 2,4-dinitrophenylhydrazone and a thiosemicarbazone.

All this taken together indicates that the addition of acetoacetic ester takes place with the opening of the oxide ring of the ethylene group of I with the formation of 1-acetyl-2(3)-(3',4'-epoxycyclohexyl)butyrolactone (IIa, b), which exists as an equilibrium mixture with the enolic form (IIIa, b):

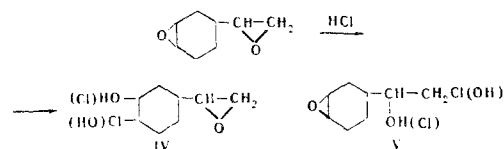


The value of the molecular refraction found for the product of the addition of acetoacetic ester to I (55.07) is between the theoretically calculated refractions for the ketonic and enolic forms.

In addition to the main product of the interaction of acetoacetic ester with I, a lower-boiling substance with the composition $\text{C}_{10}\text{H}_{18}\text{O}_3$ was isolated, this being the product of the reaction of the vinylcyclohexene dioxide with ethanol [3].

As acid reagents, we used hydrogen chloride and bromide in ethereal solution. As is well known, hydrogen halides readily react with α -oxides to form halohydrins [4, 5].

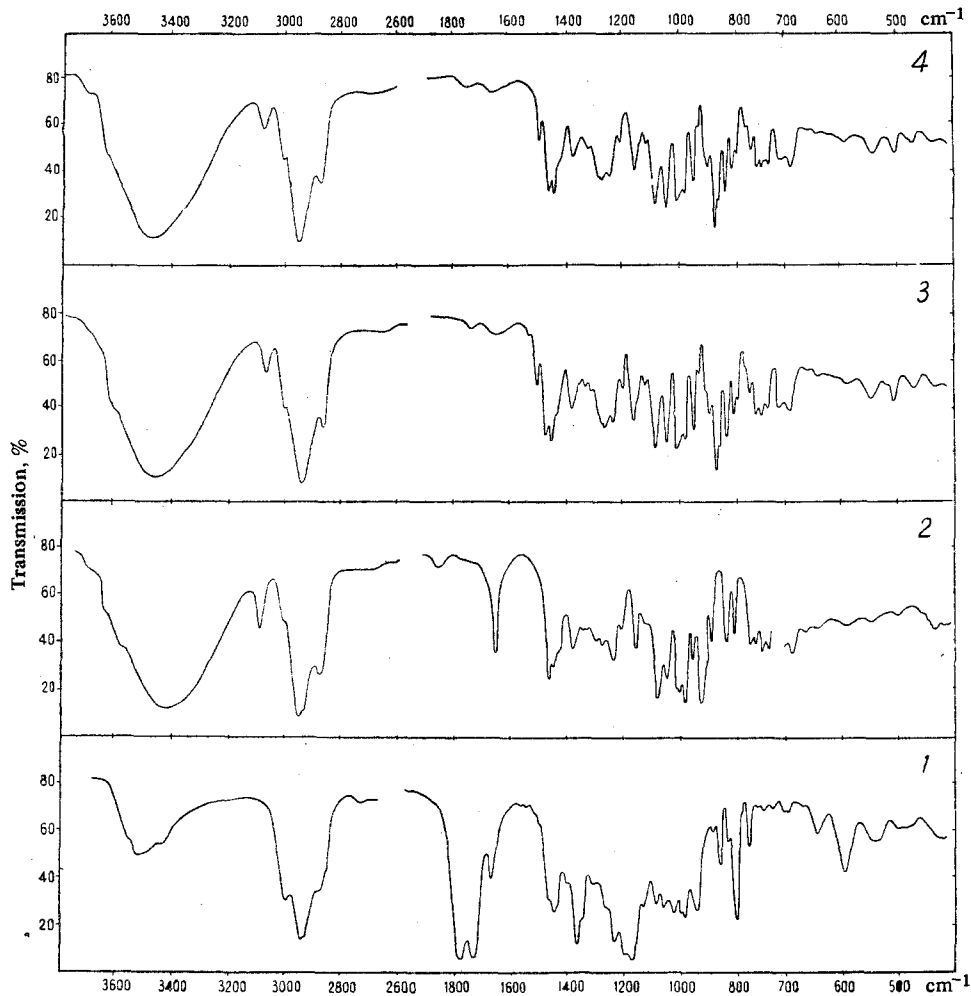
The reaction of the dioxide with hydrogen chloride was studied in more detail. It was found that the constants of the reaction products (table) differed according to the experimental conditions (temperature, amount of solvent). This can be explained by a change in the ratio of the isomers IV and V in the reaction products:



We did not investigate possible stereoisomers in the reaction products.

The order of addition of HCl to vinylcyclohexene dioxide was determined on the basis of a study of the

*For communication II, see [1].



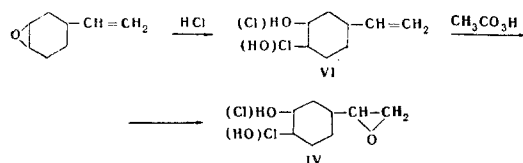
IR spectra: 1) 1-acetyl-2(3)-(3',4'-epoxycyclohexyl)butyrolactone;
2) 4(3)-chloro-3(4)-hydroxy-1-vinylcyclohexane (VI); 3) 4(3)-
chloro-1-epoxyethyl-3(4)-hydroxycyclohexane (IV), reference
sample; 4) 4(3)-chloro-1-epoxyethyl-3(4)-hydroxycyclohexane,
product of expt. No. 2 (the experimental conditions are given in
the table).

Properties of Compounds Synthesized by the Reaction of 1-Vinyl-3-cyclohexene Dioxide with Hydrogen Chloride and Bromide

Experiment no.	Reactant	Reaction conditions				Content of isomers with epoxyethyl groups, %	Bp, °C (mm)	d ₄ ²⁰	n _D ²⁰	Empirical formula	Found			Calculated			Yield, %
		molar ratio of dioxide to hydrogen halide	concentration of ethereal solution of hydrogen halide, N	maximum temperature, °C	time of the reaction (temperature, °C)						C, %	H, %	MR _D	C, %	H, %	MR _D	
1	HCl					100	113 (2)	1.2209	1.5040	C ₈ H ₁₃ ClO ₂	54.72	7.16	42.84	54.72	7.16	42.84	50.0
2	HCl	1 : 1.2	0.2	20	1 hr 10 min (15--18)	85	95--96 (0.03)	1.2216	1.5038		54.48	7.46	42.78	54.38	7.31	42.78	69.3
3	HCl	1 : 1.3	0.3	31	3 hr (20)	55	94 (0.02)	1.2281	1.5070		54.44	7.41	42.70				44.1
4	HCl	1 : 2.3	0.3	25	3 hr (20)	—	132--134 (0.007)	1.2918*	1.5140*	C ₈ H ₁₁ Cl ₂ O ₂	45.50	6.69	49.66	45.08	6.62	49.73	39.9
5	HBr	1 : 1	0.2	26	3 hr (20)	60	98--99 (0.02)	1.4958	1.5309		C ₈ H ₁₃ BrO ₂	43.55	5.97	45.71	43.46	5.92	45.68

*The refractive index and density were determined at 65° C.

IR absorption spectra by measurements of the peak intensities of the band with $\nu_{\text{as}} = 3050 \text{ cm}^{-1}$ of the terminal epoxy ring, using the Lambert-Beer law [1]. To determine the absorption coefficient k_{ν} , the reference compound 3(4)-chloro-1-epoxyethyl-3(4)-hydroxycyclohexane (IV) was obtained by the following route:



The presence in the IR spectrum of VI (figure) of the peaks at $\nu_{\text{C}=\text{C}} = 1650 \text{ cm}^{-1}$ (m), $\nu_{\text{C}-\text{H}} = 3080 \text{ cm}^{-1}$ (m), and the bands at 922 and 982 cm^{-1} (nonplanar deformation vibration of CH bonds), which are characteristic for the vinyl group, indicates that the first stage of the reaction involves the opening of the epoxy ring and not the addition of the HCl to the double bond [7].

The constants of IV are shown in the table and the IR spectrum is given in the figure.

The results of the measurements of the amount of IV in the product of the reaction of I with HCl are given in the table. It can be seen that with a high dilution of the reaction mixture with ether (0.2 N HCl solution) and at a lower temperature of the reaction mixture, the constants of the reaction product are close to those of the model compound IV, the results indicating 85% of compound IV (see curves 3 and 4, figure). When a more concentrated ethereal solution of HCl (0.3 N) was used and the reaction mixture was heated to a higher temperature (31° C) with approximately the same ratios of the reactants, the refractive index and the density rose and the ratio of the isomers IV and V became 55 : 45. When the amount of hydrogen chloride was increased to 2.3 mole per mole of dioxide I, the two oxide rings reacted simultaneously.

Thus, as in the case of the addition of alcohols and α -chloro ethers in an acid medium [1], the reaction conditions have a great influence on the order of addition of hydrogen chloride to 1-vinyl-3-cyclohexene dioxide. The milder the conditions the greater is the extent to which the HCl adds to the oxide ring of the six-membered carbon ring of the dioxide, and the more severe the conditions the lower is the selectivity of the addition of HCl.

EXPERIMENTAL

Reaction of sodioacetoacetic ester with 1-vinyl-3-cyclohexene dioxide (I). To the sodioacetoacetic ester prepared from 5 g (0.217 g-atom) of Na in 75 ml of ethanol and 34.8 g (0.268 mole) of acetoacetic ester was added 25 g (0.178 mole) of I prepared as described previously [3]. The contents of the reaction flask were heated with stirring at 55° C for 3.5 hr. On the following day, the alcohol was removed by suction filtration, and the reaction mixture was treated with 43 ml of 35% acetic acid and was then diluted with water and extracted with ether. The ethereal extract was washed with water and dried with magnesium sulfate. After the ether had been driven off, the product was distilled twice in vacuum. Two fractions were collected:

(1) 6.5 g (19.6%) of a substance with the following constants: bp 92–93° (0.007 mm); $d_4^{20} 1.0919$; $n_D^{20} 1.4811$. Found, %: C 64.66; 64.72; H 9.74; 9.81; $MR_D 48.54$. Calculated for $C_{11}H_{18}O_3$, %: C 64.48; H 9.74; $MR_D 48.79$. (2) 5.2 g (13%) of a product with bp 135–136.5° (0.007 mm); $d_4^{20} 1.1986$; $n_D^{20} 1.5009$. Found, %: C 64.27; 64.21; H 7.59; 7.44; $MR_D 55.07$. Calculated for $C_{12}H_{16}O_4$, %: C 64.27; H 7.19; MR_D (ketonic form) 54.32; MR_D (enolic form) 55.37. The substance decolorized potassium permanganate solution and gave a dark violet coloration with ferric chloride. The 2,4-dinitrophenylhydrazone and thiosemicarbazone were prepared but could not be purified by recrystallization, since when this was attempted uncrystallizable oils were deposited.

Action of hydrogen halides on 1-vinyl-3-cyclohexene dioxide (I). With stirring, 0.139–0.085 mole (0.264 mole in experiment No. 4, table) of a 0.2–0.3 N ethereal solution of hydrogen halide was added to 0.107–0.086 mole of the dioxide. By means of ice water cooling the temperature was not allowed to rise above the figure given. After three hours' standing at 20° C (1 hr 10 min at 15–18° C in experiment No. 2, table), the reaction mixture was treated with 7% potassium hydroxide solution and washed with water. The ethereal layer was dried over magnesium sulfate. After the ether had been driven off, the produce was distilled twice in vacuum. The constants of the products obtained and their percentage contents of the isomers with the epoxyethyl group in each experiment are given in the table.

4(3)-Chloro-1-epoxyethyl-3(4)-hydroxycyclohexane (IV). At room temperature, 1.16 l of a 0.2 N ethereal solution of hydrogen chloride ($T_{\text{HCl}} = 0.00729$), corresponding to 8.5 g (0.233 mole) of HCl was added dropwise to 28.9 g (0.233 mole) of the dioxide I. After being left at room temperature for 3 hr, the reaction mixture was treated as described above. Two distillations gave 29.1 g (77.8%) of the chlorocyclohexane VI with the following constants: bp 100–100.5° (8 mm); $d_4^{20} 1.1067$; $n_D^{20} 1.5008$. Found, %: C 59.72; 59.43; H 8.25; 8.19; Cl 21.96; 21.86; $MR_D 42.87$. Calculated for $C_8H_{13}ClO_2$, %: C 59.81; H 8.15; Cl 22.07; $MR_D 42.87$.

23.6 g (0.147 mole) of VI in 59 ml of ether was oxidized [8] with 17 ml of 84.2% acetyl hydroperoxide. Two distillations yielded 13.0 g (50.0%) of the chlorocyclohexane IV, the constants of which are given in the table.

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