INVESTIGATIONS IN THE FIELD OF THE REACTIONS OF CYCLENE α-OXIDES

V. Reaction of 1-Vinylcyclohex-3-ene Dioxide with Carboxylic Acids*

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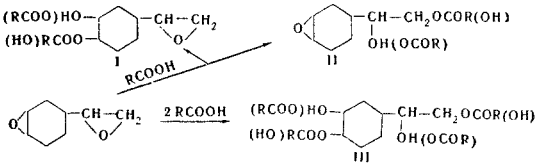
The reaction of 1-vinylcyclohex-3-ene dioxide with carboxylic acids (acetic, propionic, butyric, and monochloroacetic) is described. On the basis of IR spectra, it has been shown that in the reactions without a catalyst the carboxylic acids add mainly to the epoxyethyl group of the molecule of the dioxide, while in the presence of $FeCl_3$ as catalyst a mixture of isomers with epoxyethyl and epoxycyclohexane groups in a ratio of 55 : 54 is obtained.

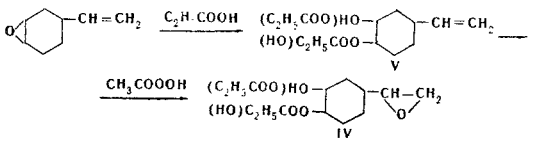
On the basis of a study of the IR absorption spectra, we have shown previously [1-5] that the epoxide rings of 1-vinylcyclohex-3-ene dioxide have different reactivities according to the type of reagent and the reaction conditions.

It is known from the literature that carboxylic acids occupy an intermediate position in relation to nucleophilic and electrophilic reagents [6]. In view of this, it appeared of interest to investigate the reaction of carboxylic acids (acetic, propionic, butyric, and monochloroacetic) with 1-vinylcyclohex-3-ene dioxide. The reaction of α-olefin oxides with carboxylic acids has been well studied [7]. The addition of carboxylic acids to dioxides of cycloolefins has not been reported in the literature. The reaction of carboxylic acids with 1-vinylcyclohex-3-ene dioxide may be expected to form the following products:



The reactions were carried out both in the absence of a catalyst and in the presence of the catalyst ferric chloride. The constants of the reaction products are given in Table 1.

The influence of the reaction conditions on the position of the addition of the carboxylic acid to 1-vinylcyclohex-3-ene dioxide was studied in the greatest detail in the case of the action of propionic acid. Using IR spectroscopy [8], on the basis of the Lambert-Beer law ($\log I_0/I = K_\nu \cdot c \cdot d$) a quantitative determination of the amounts of isomers with epoxyethyl and epoxycyclohexane groups in the products of the reaction of the dioxide with propionic acid was made. The model compound 1-epoxyethyl-3-hydroxy-4-propionyloxycyclohexane (or the corresponding 4-hydroxy-3-propionyloxy compound) (IV), used to find the absorption coefficient K_ν 3050 cm^{-1}, was obtained by the following route:



*For part IV, see [4].

Table 1

Properties of the Compounds Synthesized by the Action of Carboxylic Acids on 1-Vinylcyclohex-3-ene Dioxide

Acid added	Catalyst	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Empirical formula	C, % found	C, % calculated	H, % found	H, % calculated	Yield, %
CH_3COOH	—	104.5—106 (0.006)	1.4860	1.1821	48.61	48.80	$C_{10}H_{16}O_4$	60.12 60.49	59.98	8.13 8.27	8.05	62.0
CH_3COOH	$FeCl_3$	108—109.5 (0.03)	1.4850	1.1784	48.70	48.80	$C_{10}H_{16}O_4$	59.87 59.59	59.98	7.92 7.78	8.05	10.7
C_2H_5COOH	—	109—111 (0.007)	1.4825	1.1477	53.27	53.42	$C_{11}H_{18}O_4$	61.50 61.83	61.66	8.58 8.68	8.47	52.4
C_2H_5COOH	$FeCl_3$	113—114 (0.04)	1.4799	1.1366	53.55	53.42	$C_{11}H_{18}O_4$	61.66 61.31	61.66	8.53 8.46	8.47	21.2
C_2H_5COOH (model compound)	—	115—116 (0.04)	1.4769	1.1304	53.57	53.42	$C_{11}H_{18}O_4$	61.39 61.32	61.66	8.48 8.46	8.47	42.6
C_3H_7COOH	—	114—115 (0.007)	1.4804	1.1200	57.95	58.04	$C_{12}H_{20}O_4$	62.69 62.67	63.13	8.80 8.75	8.83	50.0
C_3H_7COOH	$FeCl_3$	116—118 (0.03)	1.4787	1.1162	57.97	58.04	$C_{12}H_{20}O_4$	62.81 62.90	63.13	8.78 8.82	8.83	41.2
		160—162 (0.03)*	1.4770	1.1084	80.72	80.25	$C_{16}H_{28}O_4$	60.33 60.57	60.74	8.75 8.73	8.92	8.2
$ClCH_2COOH$	—	127—129 (0.01)	1.5062	1.3079	53.34	53.67	$C_{10}H_{15}ClO_4$	50.79 50.72	51.18	6.34 6.53	6.44	37.3

*Constants of the products of addition of 2 moles of the acid.

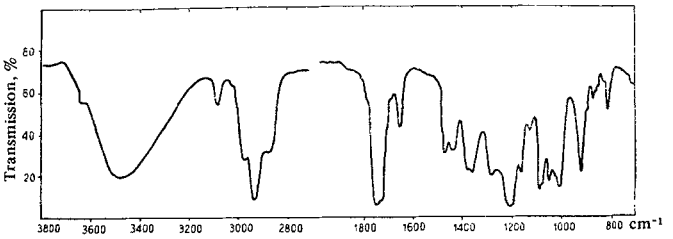


Fig. 1. IR spectrum of 3-hydroxy-4-propionyloxy-1-vinylcyclohexane (or the corresponding 4-hydroxy-3-propionyloxy compound) (V).

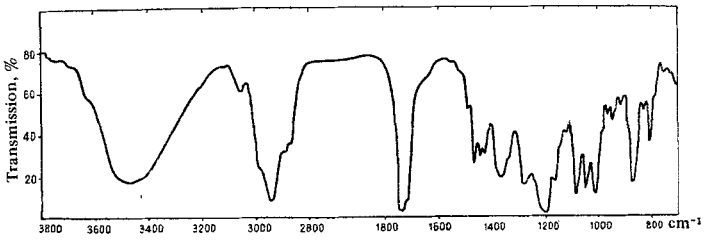


Fig. 2. IR spectrum of 1-epoxyethyl-3-hydroxy-4-propionyloxycyclohexane (or the corresponding 4-hydroxy-3-propionyl compound) (IV).

The IR spectrum of V (Fig. 1) had characteristic frequencies of a vinyl group: $\nu_{C=C}$ 1650 cm^{-1}; ν_{C-H} 3082 cm^{-1}; and 920 and 1002 cm^{-1} — the non-planar deformation vibrations of C—H bonds—which confirms this structure.

In the IR spectrum of IV (Fig. 2), the frequencies of the vinyl group were absent and the band of an epoxyethyl group $\nu_{as}CH_2$ had appeared at 3050 cm^{-1}. Table 2 shows the dependence of the content of the isomers with the epoxyethyl group in the reaction product on the conditions of performing the experiments.

In the reaction of equimolar amounts of the dioxide and monochloroacetic acid in a solvent (toluene–dioxane), just as in the experiment with propionic acid, addition takes place mainly to the epoxyethyl group. The content of 1-epoxyethyl-3-hydroxy-4-chloracetoxycyclohexane (or the corresponding 4-hydroxy-3-chloroacetoxy compound) (I, R = CH_2Cl) was only 10%.

The product of the addition of 2 moles of the acid (III, R = C_3H_7) was isolated only in the experiment with butyric acid. Its constants are given in Table 1.

EXPERIMENTAL

1-Vinylcyclohex-3-ene dioxide. This was obtained by oxidizing 1-vinyl-cyclohex-3-ene with acetyl hydroperoxide by Arbuzov's method and had the following constants: bp 97–99° C (9 mm); d_4^{20} 1.0967, n_D^{20} 1.4782.

Action of carboxylic acids on 1-vinylcyclohex-3-ene dioxide without a catalyst. To 0.05–0.07 mole of the dioxide was added 0.20–0.28 mole of the appropriate acid. The reaction mixture was heated with stirring at 65–70° C for 5 hr. On the following day the excess of acid was distilled off and the product was twice distilled in vacuum. The constants of the substances obtained are given in Table 1.

Action of carboxylic acids on 1-vinylcyclohex-3-ene dioxide in the presence of ferric chloride. A mixture of 0.10–0.18 mole of the dioxide and 0.30–0.54 mole of the corresponding acid was treated with 0.2–0.3 g of ferric chloride. The temperature rose to 43° C in the experiment with acetic acid and to 25–29° C in those with propionic and butyric acids. After this, the reaction mixture was heated at 55–60° C for 2 hr and was then treated with 7% caustic potash solution and extracted with ether. The ethereal extracts were washed with water and dried over magnesium sulfate. The ether was driven off and the product was twice distilled in vacuum. The constants of the substances obtained are given in Table 1.

Action of chloroacetic acid. A solution of 10.1 g (0.11 mole) of monochloroacetic acid in a mixture of 40 ml of absolute toluene and 5 ml of dioxane was treated with 15 g (0.11 mole) of the dioxide. The temperature rose to 30° C, and after this the reaction mixture was kept at 30° C for 1 hr. Then the solvent was driven off and the product was distilled in vacuum, giving 9.1 g (37.3%) of a substance the constants of which are given in Table 1.

Synthesis of the model compound. **A) Preparation of 3-hydroxy-4-propionyloxy-1-vinylcyclohexane (or the corresponding 4-hydroxy-3-propionyloxy compound)(V).** A mixture of 25 g (0.20 mole) of 3,4-epoxy-1-vinylcyclohexane and 44.7 g (0.60 mole) of propionic acid was heated with stirring at 65° C for 3 hr. On the following day the excess of propionic acid was distilled off and the product was distilled in vacuum. After a second distillation, 12.0 g (30.1%) of a substance with the following constants was obtained: bp 83–84° C (0.3 mm); d_4^{20} 1.0421; n_D^{20} 1.4740. Found, %: C 66.89, 66.55, H 9.05; MR_D 53.51. Calculated for $C_{11}H_{18}O_3$, %: C 66.64, H 9.15; MR_D 53.51, %: A fraction with bp 130–150° C (0.04 mm) (8.2 g) was also obtained from which no individual products could be obtained on redistillation.

B) Preparation of 1-epoxyethyl-3-hydroxy-4-propionyloxycyclohexane (or the corresponding 4-hydroxy-3-propionyloxy compound)(IV). A solution of 14.3 g (0.072 mole) of V in 30 ml of absolute ether was treated with 8.4 ml of 85.7% acetyl peroxide (30% excess). After it had been allowed to stand at room temperature for 7 days, the mixture was treated with 7% caustic potash solution, washed with water, and dried over magnesium sulfate. After the elimination of the ether, the product was distilled in vacuum. Two distillations yielded 6.6 g (42.6%) of a substance the constants of which are given in Table 1.

Table 2

Conditions of the Reaction of Propionic Acid with 1-Vinylcyclohex-3-ene Dioxide.

Catalyst	Molar ratio of dioxide to acid	Content of the isomers with the epoxyethyl group, %
—	1 : 1 (in benzene)	10
—	1 : 4	30
$FeCl_3$	1 . 3	55
—	Model compound	100

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