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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UDC 547.717+547.59:543.422:542.95

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 FeCl₃ as catalyst a mixture of isomers with epoxyethyl and epoxycyclohexane groups in a ratio of 55:44 is obtained.

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.

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:

\[
\text{(RCOO)H} = \text{O} - \text{CH} = \text{C} - \text{H} - \text{CH}_2 - \text{OCOR(OH)}_2
\]

\[
\text{HO} = \text{C} - \text{CH} - \text{CH}_2 - \text{O} - \text{C} - \text{R}_2
\]

\[
\text{HO} = \text{C} - \text{CH} - \text{CH}_2 - \text{O} - \text{C} - \text{R}_2
\]

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 \( \log \frac{I_0}{I} = k \rho \cdot c \cdot d \) 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 \( K \), was obtained by the following route:

\[
\text{CH}_3 \text{COOOH (CH}_3 \text{COO)}_2 \text{H} = \text{O} - \text{C} - \text{CH} = \text{C} - \text{H} - \text{CH}_2 - \text{OCOR(OH)}_2 \\
\text{HO} = \text{C} - \text{CH} - \text{CH}_2 - \text{O} - \text{C} - \text{R}_2
\]

Table 1

<table>
<thead>
<tr>
<th>Acid added</th>
<th>Catalyst</th>
<th>Bp. °C (pressure, mm)</th>
<th>( n_2^\text{D} )</th>
<th>( d_2^\text{D} )</th>
<th>MP, °C</th>
<th>Empirical formula</th>
<th>C, %</th>
<th>H, %</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COOH</td>
<td></td>
<td>104.5—106 (0.006)</td>
<td>1.4860</td>
<td>1.1821</td>
<td>48.61</td>
<td>C₆H₁₀O₄</td>
<td>60.12</td>
<td>60.49</td>
<td>8.13</td>
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<tr>
<td>CH₂COOH</td>
<td>FeCl₃</td>
<td>108—109.5 (0.03)</td>
<td>1.4850</td>
<td>1.1784</td>
<td>48.70</td>
<td>C₆H₁₀O₄</td>
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<td>59.59</td>
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<tr>
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<td>109—111 (0.007)</td>
<td>1.4825</td>
<td>1.1477</td>
<td>53.27</td>
<td>C₇H₁₂O₄</td>
<td>61.50</td>
<td>61.86</td>
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<tr>
<td>C₄H₄COOH</td>
<td>FeCl₃</td>
<td>113—114 (0.04)</td>
<td>1.4799</td>
<td>1.1366</td>
<td>53.55</td>
<td>C₇H₁₂O₄</td>
<td>61.66</td>
<td>61.31</td>
<td>8.53</td>
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<tr>
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<td>115—116 (0.04)</td>
<td>1.4769</td>
<td>1.1304</td>
<td>53.57</td>
<td>C₈H₁₆O₄</td>
<td>61.39</td>
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<td>8.48</td>
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<tr>
<td>C₆H₄COOH</td>
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<td>114—115 (0.007)</td>
<td>1.4804</td>
<td>1.1200</td>
<td>57.95</td>
<td>C₈H₁₆O₄</td>
<td>62.69</td>
<td>63.13</td>
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<tr>
<td>C₇H₄COOH</td>
<td>FeCl₃</td>
<td>115—118 (0.03)</td>
<td>1.4787</td>
<td>1.1162</td>
<td>57.97</td>
<td>C₈H₁₆O₄</td>
<td>62.81</td>
<td>63.13</td>
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<td>1.4770</td>
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<td>80.72</td>
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<td>1.3079</td>
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<td>C₉H₁₈O₄</td>
<td>50.79</td>
<td>50.72</td>
<td>6.34</td>
</tr>
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</table>

*For part IV, see [4].

*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-propionyloxy-cyclohexane (or the corresponding 4-hydroxy-3-propionyl compound) (IV).