FREE RADICAL ADDITION OF CARBOXYLIC ESTERS
TO UNSATURATED EPOXY COMPOUNDS

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The addition reaction of carboxylic esters at a carbon-carbon double bond, initiated by peroxides,
has been extensively studied in its application to alkenes and various unsaturated compounds which have
functional groups and heteroatoms in their structure. Based on this reaction, synthesis methods have been
found for branched mono- and dicarboxylic acids [1-3], hydroxy and oxy acids [4, 5], and also carboxylic
acids containing phenyl, cyclohexyl, and cyclopentyl rings [6-8]. The introduction of a functional group
into a hydrocarbon molecule, as a rule, complicates the homolytic process taking place in a reacting sys-
tem. Such molecules, to a greater extent than alkenes, are prone to secondary kinetic chain termination
reactions by homolysis of the adjacent C-H bonds activated by the functional group, with subsequent re-
combination or disproportionation of the radicals formed.

In the present work, to examine the possibility of free radical synthesis of epoxy compounds con-
taining an ester group of atoms, the addition of carboxylic esters to unsaturated epoxides, initiated by di-
tertiary butyl peroxide (DTBP), was accomplished:

\[ \text{CH}_2\text{CH}\text{CH}_2\text{OCH}_2\text{C}+\text{CH}=\text{CH}_2+\text{nCH}_2\text{COOR} \rightarrow \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{C} \text{H}_2\text{CHCOOR} \]  

The starting materials, the resulting 1:1 adducts, and their properties are shown in Table 1. The structure
of the 1:1 adducts is in keeping with the mechanism of the reaction and is confirmed by the IR spectra. In
the IR spectra of the compounds listed there are absorption bands characteristic of an epoxy group in the
ranges 840-860, 890-910, 1250-1260, and 3040-3050 cm\(^{-1}\). The bands in the range 1740-1750 cm\(^{-1}\) corre-
spond to the ester grouping in the compounds (expts. 1-6), at 1770 cm\(^{-1}\) to a five-membered lactone (expt.
7). Also, the appreciable absorption characteristic of compounds with a hydroxyl group (3300-3600 cm\(^{-1}\)) is missing from the spectra. The substances were plotted in a thin layer on a UR-10 instrument. The ac-
curacy of the system shown above was further confirmed, using as an example the determination of the
structure of the adduct prepared from butyrolactone and 1,2-epoxy-4-oxahept-6-ene (expt. 7). By the ac-
tion of hydrogen chloride this adduct was converted to the corresponding chlorohydrin - \( \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{C}+\text{CH}=\text{CHCH}_2\text{OH} \rightarrow \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{C}+\text{CH}=\text{CHCH}_2\text{OH} \)

Both specimens had identical physical properties (including the IR spectra). The constitution of the epi-
chlorohydrin, the synthesis of which was carried out according to reactions (2) and (3), is in no doubt. It
was previously established that the addition of butyrolactone to unsaturated compounds under the action of

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article submitted April 2, 1969.
<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Addend</th>
<th>( R_1 + \text{O} ) (mm Hg)</th>
<th>Bp. (°C)</th>
<th>Calcd. %</th>
<th>Found %</th>
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<tbody>
<tr>
<td>1</td>
<td>( \text{CH}_2-\text{COOCH}_3 )</td>
<td>124-126</td>
<td>77.32</td>
<td>51.84</td>
<td>51.37</td>
</tr>
<tr>
<td>2</td>
<td>( \text{CH}_2-\text{COOCH}_3 )</td>
<td>138-141</td>
<td>77.18</td>
<td>56.24</td>
<td>56.49</td>
</tr>
<tr>
<td>3</td>
<td>( \text{CH}_2-\text{COOCH}_3 )</td>
<td>127-129</td>
<td>71.13</td>
<td>63.18</td>
<td>63.56</td>
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<tr>
<td>4</td>
<td>( \text{NO}_2-\text{COOCH}_3 )</td>
<td>138-141</td>
<td>77.18</td>
<td>51.84</td>
<td>51.37</td>
</tr>
<tr>
<td>5</td>
<td>( \text{CH}_2-\text{COOCH}_3 )</td>
<td>149-152</td>
<td>71.13</td>
<td>63.18</td>
<td>63.56</td>
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<tr>
<td>6</td>
<td>( \text{CH}_2-\text{COOCH}_3 )</td>
<td>149-161</td>
<td>77.18</td>
<td>51.84</td>
<td>51.37</td>
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<tr>
<td>7</td>
<td>( \text{CH}_2-\text{COOCH}_3 )</td>
<td>149-161</td>
<td>77.18</td>
<td>51.84</td>
<td>51.37</td>
</tr>
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</table>

*In the unreacted epoxy compound was 1,2-epoxy-2-methylpent-4-ene and in the remaining experiments it was 1,2-epoxy-4-oxahex-5-ene.*