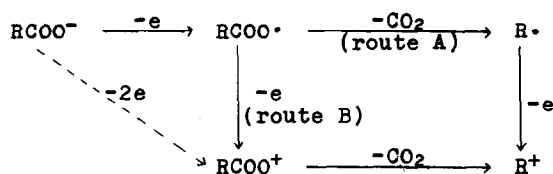


SMALL RING COMPOUNDS XXIII  
STEREOCHEMISTRY OF THE RING OPENING  
IN THE ANODIC OXIDATION OF CYCLOPROPANECARBOXYLIC ACIDS

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Two different reaction mechanisms (routes A and B) have been conceived for the generation of a cationic intermediate in the anodic decarboxylation of a carboxylic acid<sup>1)</sup>.



The essential difference in these two pathways consists in the stage at which the second electron is transferred from the reactant to the anode. Sufficient chemical evidences for the establishment of the reaction mechanism have not been reported as yet.

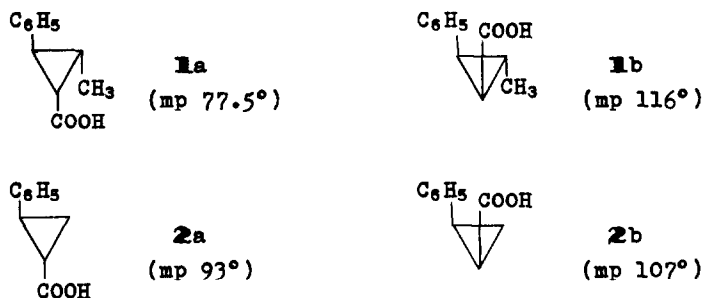
In the present communication, we wish to report an evidence which suggests the generation of the acyloxonium ion in the anodic decarboxylation reaction.

In the solvolytic reactions of cyclopropyl halides or some esters of cyclopropanols, cyclopropyl cations are not the reaction intermediates but the cyclopropane ring is opened concertedly with the elimination of the leaving anionic group yielding stereospecific products<sup>2)</sup>.

In the anodic decarboxylation reaction of cyclopropanecarboxylic acids, the route A yields cyclopropyl radicals and cyclopropyl cations.

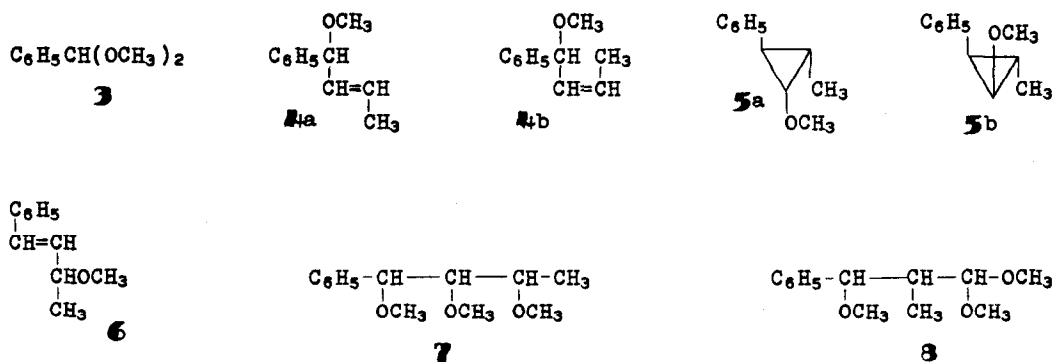
Generally, cyclopropyl radical does not retain its stereoconfiguration and does not yield ring opened products at low reaction temperature<sup>3)</sup>, and the cation gives nonstereospecific allylic products<sup>4)</sup>.

On the other hand, in the reaction route B, the elimination of carbon dioxide from the intermediate cyclopropanecarboxonium ion must result in the concerted ring opening of the cyclopropane ring yielding stereospecific allylic products. Compounds **1a**<sup>5)</sup>, **b** and **2a**<sup>6)</sup>, **b** were used as the starting carboxylic acids.



The electrolysis was carried out with carbon electrodes at -30°~-40° in methanol containing sodium methoxide as a supporting electrolyte. Supplied terminal voltage was 35~40v. and current was 0.5A.

Compounds **3**; **4a, b**; **5a, b**; **6**; **7**; **8** and two unidentified polymethoxylated products were obtained from the anodic oxidation of **1a, b**. The reaction was carried out until about 35~40% of the starting carboxylic acid was consumed. All of the products were identified by spectroscopic methods and gas chromatographic technique.

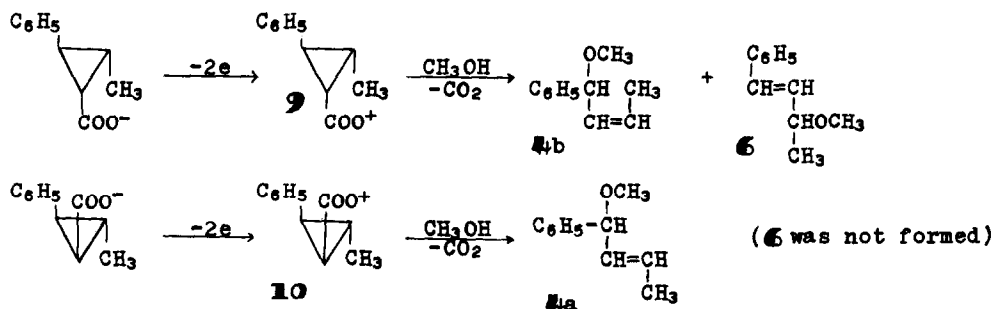


The distributions of the products were as follows.

From **1a**; **3** 8.0; **4a** 0; **4b** 22.1; **5a** 0.4; **5b** 0.1; **6** 10.9; **7** 23.3; **8** 13.1;  
unidentified products, total 22.1.

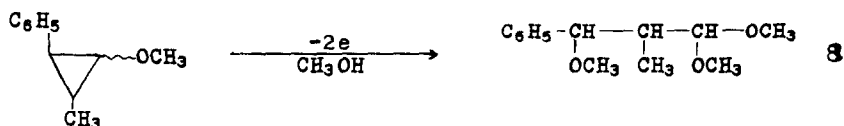
From **1b**; **3** 4.5; **4a** 6.4; **4b** 0; **5a** 9.2; **5b** 2.4; **6** 0; **7** 18.5; **8** 25.3;  
unidentified products, total 33.7.

The experimental results indicated that the allylic products **4a,b** and **6** were formed through concerted stereospecific ring opening of cyclopropane ring.



The formation of the cis isomer of **6** from **1b** is uncertain.

However, the sterically unfavorable configuration of the cis isomer of **6** may make the formation of the isomer disadvantageous. Compounds **7** and **8** are the secondary products, and the former was yielded from **4a,b** and **6**, and the formation of the latter compound from **5a,b** was confirmed by the electrolyses of the ethers under the similar reaction condition.



That the total yield of **5a,b** and **8** from **1b** is much higher than that from **1a** may be elucidated by the presumption that the concerted ring opening of **10** is less favorable by the steric interaction and hence **5a,b** is favorably formed from **10** without ring opening.

The electrolysis of **2a,b** under the same reaction condition gave a similar result which supports the formation of the acyloxonium ion and subsequent concerted ring opening of the cation.

The retention of stereoconfiguration of cyclopropyl radicals is requisite to elucidate the experimental results by route A. In the studies of Kolbe electrolysis, however, the retention of stereoconfiguration of the intermediate radical by stereospecific adsorption of the radical on the surface of the anode has not been observed<sup>7</sup>). Consequently, the experimental results suggest that the main reaction pathway of the anodic decarboxylation reaction of cyclopropanecarboxylic acids is the route B characterized by the formation of the acyloxonium ion, although the formation of the cyclopropyl radical (route A) could not be denied. The reaction route B, however, might be operative to only the anodic decarboxylation of cyclopropanecarboxylic acids, since the difficulty of the formation of a cyclopropyl radical may make the decarboxylation of the cyclopropanecarboxy radical unfavorable reaction. Further study on the anodic reaction of cyclopropanecarboxylic acids is in progress.

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