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SMALL RING COMPOUNDS XXVI

STEREOCHEMISTRY IN THE OXIDATIVE DECARBOXYLATION OF CYCLOPROPANECARBOXYLIC ACIDS WITH LEAD TETRAACETATE

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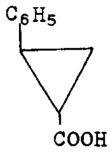
It has been reported in the previous study[1] that the anodic decarboxylation of 2-phenylcyclopropanecarboxylic acid gave stereospecific ring opened products suggesting that the anodic oxidation reaction proceeds according to the following route B characterized by the generation of acyloxonium ion.

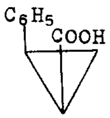
$$\begin{tikzcd}
RCOO^- \arrow[r, "-e"] \arrow[dr, dashed, "-2e"'] & RCOO\cdot \arrow[r, "\overset{\text{(route A)}}{-CO_2}"] \arrow[d, "\begin{matrix}-e\\ \text{(route B)}\end{matrix}"] & R\cdot \arrow[d, "-e"] \\
 & RCOO^+ \arrow[r, "-CO_2"] & R^+
\end{tikzcd}$$

The formation of acyloxonium ion might be a distinctive feature of the anodic oxidation of carboxylic acid or it might be resulted from the cyclopropane ring strain which may obstruct the decarboxylation of cyclopropanecarboxy radical.

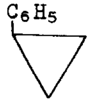
In the present study, the oxidative decarboxylation of 2-phenylcyclopropane carboxylic acid by lead tetraacetate was carried out to investigate the difference between anodic and chemical oxidation mechanisms. Trans and cis 2-phenylcyclopropane carboxylic acids (**I**a,**I**b) were used as the starting compounds, and the solution of **I**a,b in anhydrous benzene containing cupric acetate and pyridine as catalysts was treated with lead tetraacetate at reflux temperature under an atmosphere of nitrogen. Following products,**2**∼**7**, were obtained in moderate yields (55∼58%).



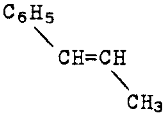
1a



1b



2



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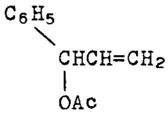
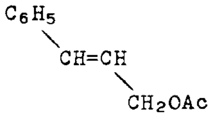
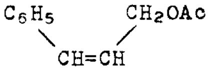


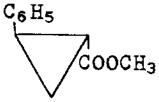
4



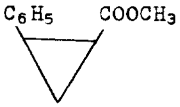
5a



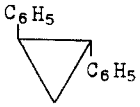
5b



6a



6b



7a

All of the products were identified by the comparisons of their spectroscopic and gaschromatographic behaviors with those of authentic samples. The distributions of the products were indicated in Table I. The stereospecific ring opening must give **5**a from **1**a and **5**b from **1**b.

Table I The distribution of the products (%)

Starting Compound	**2**	**3**	**4**	**5**a	**5**b	**6**a	**6**b	**7**a
1a	2.2	1.3	13.3	24.6	1.8	29.5	0	27.3
1b	4.6	3.1	15.3	29.9	3.5	0	17.7	25.9

Compounds **5**a,b retained their stereoconfigurations under the reaction condition. Thus, the result that trans compound, **5**a was given almost exclusively from both cis and trans acids would suggest that compounds **5**a,b, the products formed from cationic intermediate, were yielded by non-stereospecific ring opening of the starting compounds.

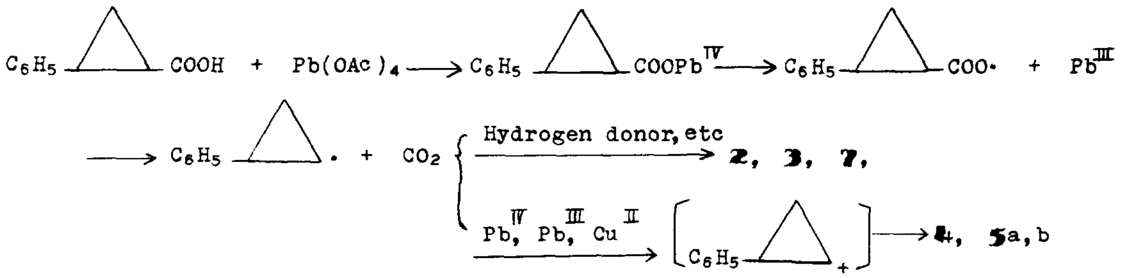
The mechanism of oxidation of carboxylic acid by lead tetraacetate still remains some uncertainties[2]. The generation of cationic species in this oxidation reaction has been explained by two different mechanisms, (1) and (2)[3][4].

$$\left.\begin{array}{llll} RCOOPb^{IV} \longrightarrow & RCOO^{+} & + & Pb^{II} \\ RCOO^{+} \longrightarrow & R^{+} & + & CO_2 \end{array}\right\} \quad (1)$$

$$\left.\begin{array}{l} RCOOPb^{IV} \longrightarrow R\cdot + CO_2 + Pb^{III} \\ RCOOPb^{III} \longrightarrow R\cdot + CO_2 + Pb^{II} \\ R\cdot + Pb^{IV} \text{ or } Pb^{III} \longrightarrow R^{+} + Pb^{III} \text{ or } Pb^{II} \end{array}\right\} \quad (2)$$

Acyloxonium ion intermediate is generated in the reaction route (1) and hence, according to this route, compound **5** should be yielded through the stereospecific opening of cyclopropane ring as was observed in the anodic oxidation.

On the other hand, in the reaction mechanism (2) the cationic species is formed in non-stereospecific manner[5]. It thus appeared that in the oxidative decarboxylation reaction by lead tetraacetate, the acyloxonium ion was not involved as the intermediate, but cyclopropyl radical was generated and oxidized to the cationic species by metal ion.



The non-stereospecificity in the formation of **7a** was fully in accordance with the result observed in the previous studies[6][7].

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