Tetrahedron Letters No.51, pp. 4687-4689, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE DECARBOXYLATION OF CYCLOPROPANECARBOXYLIC AND CYCLOPROPYLACETIC ACIDS

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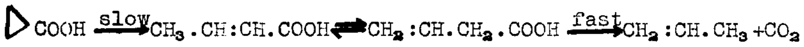
(**Received 28 October 1965**)

Two recent Communications on the decarboxylation of substituted cyclopropylacetic acids[1,2] prompt us to record our preliminary observations on the parent acids.

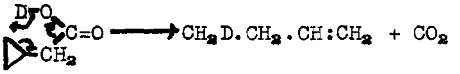
The thermal decarboxylation of $\beta\gamma$-unsaturated acids is now known to involve a cyclic transition state.[3,4,5,6] The similarity of cyclopropyl groups to double bonds in many of their reactions led us to investigate the thermal behaviour of cyclopropyl carboxylic acids where the cyclopropyl group was so disposed as to be analogous first to an $\alpha\beta$- and then to a $\beta\gamma$-unsaturated acid.

Cyclopropanecarboxylic acid, the cyclopropyl analogue of acrylic acid, decarboxylates at 390° to the extent of 60% in 16 hours (1.5 atmospheres pressure, gas phase) to give prop-1-ene, carbon dioxide and a little carbon monoxide; the residual acid was unchanged. It is stable at 290° where but-3-enoic acid readily decarboxylates.[5] On the other hand, when the same acid was partially pyrolyzed by dropping it slowly in a fast stream of nitrogen down a glass packed column at 520° (contact time ca. 1 second) there was considerable unreacted acid which proved to be largely crotonic acid, together with a little but-3-enoic acid and unchanged cyclopropanecarboxylic acid. We interpret these results on the basis of the following scheme:

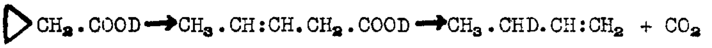


We have evidence that the interconversion of crotonic and but-3-enoic acids has an order greater than unity;[6] accordingly at high pressures the isomerization will be fast, whilst in the packed column pyrolysis, where the acid molecules are largely separated from each other, this stage will almost be stopped.

The decarboxylation of cyclopropylacetic acid may be envisaged to proceed by one or both of two paths (for brevity the decarboxylation of the deuteroacid is drawn):



........................(i)



....(ii)

At 320° in the gas phase the reaction is first order, having $k=1.1 \times 10^{-6}$ sec.$^{-1}$ This does not distinguish the two mechanisms, but is much slower than the decarboxylation of but-3-enoic acid.[5] Although the acid recovered from partial pyrolysis at 510° (packed column) appears unchanged, in accord with mechanism (i), we believe that mechanism (ii) is probably operative on the basis of studies on the deuteroacid. Although the deuterium label scrambles in liquid phase decarboxylation,[4] it appears not to do so in the gas phase. Thus dilute gas phase pyrolysis of cyclopropylacetic acid carboxyl-D gives rise to deuterobut-1-ene, together with a little but-2-ene, produced by isomerization. The N.M.R. spectrum of the deuterobut-1-ene has methyl, methylene and methine protons in the ratio 2.9:1.1:3.0. The peak corresponding to the methyl protons is a doublet containing considerable fine structure, and shows no trace of the triplet found in but-1-ene itself at the same position. As a check, pent-3-enoic acid carboxyl-D was decarboxylated under the same conditions. The N.M.R. spectrum of the resultant olefin was almost identical with that described above.

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