## Studies in Decarboxylation. Part I. The Mechanism of 742. Decarboxylation of Unsaturated Acids.

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The thermal decarboxylation of twelve unsaturated acids has been examined. Deuterium labelling and the kinetics of the reaction show the reaction to be a cyclic intramolecular process.

THE thermal decarboxylation of unsaturated acids at temperatures above 250° has long been known, but no systematic study of the reaction has yet appeared. The older literature contains many references to the reaction, but the experimental conditions vary so widely that comparison of the products and yields reported is not possible. The currently accepted mechanism of the reaction <sup>1,2</sup> rests largely on the observation <sup>3</sup> that 2,2-dimethylbut-3-enoic acid readily undergoes thermal decarboxylation whilst 4,4-dimethylpent-2-enoic acid is resistant to the same conditions. The same Paper<sup>3</sup> notes that preliminary results show the reaction to be first order. By analogy with the thermal decarboxylation of  $\beta$ -keto-acids,<sup>4</sup> a cyclic mechanism involving a six-membered transition state was put forward, the initial equilibration step already being well established: 5

 $\beta\gamma$ -Unsaturated acids give rise to olefins in which the double bond has migrated one unit along the carbon chain, whilst the position of the double bond in olefins derived from  $\alpha\beta$ unsaturated acids apparently remains unaltered. The present Paper describes experiments designed to test further the above mechanism.

## RESULTS AND DISCUSSION

Consideration of the transition state (I) leads to the following predictions: (i) when  $\mathbf{R}' = \mathbf{H}$ , a terminal olefin should result from decarboxylation, although an internal olefin would be thermodynamically more stable; (ii) when R' = alkyl, trans-olefins should be formed in preference to their *cis*-isomers; (iii) the hydrogen atom of the carboxyl group should become attached to the  $\gamma$ -carbon atom; (iv) the reaction should show first-order kinetics; and (v) the entropy of activation should be negative.<sup>6</sup> The experiments described below were designed to test the first four of these predictions; a subsequent communication concerning the effect of structure on the rate of decarboxylation will include the fifth prediction.

All twelve of the acids listed in the Table decarboxylate to give products in accord with the scheme of Arnold *et al.*<sup>3</sup> In some cases, where the resultant olefin is tri- or tetra-alkylated, stereochemical consequences cannot be drawn. In other cases, the  $\beta\gamma$ -unsaturated acid not being synthesized readily, experiments were performed on the  $\alpha\beta$ -unsaturated isomer; isomerization to the  $\beta_{\gamma}$ -unsaturated acid prior to decarboxylation was assumed. It

<sup>&</sup>lt;sup>1</sup> Hine, "Physical Organic Chemistry," 2nd edn., McGraw-Hill, New York, 1962.
<sup>2</sup> Gould, "Mechanism and Structure in Organic Chemistry," Holt Rhineheart, and Winston, New York, 1959.

 <sup>&</sup>lt;sup>3</sup> Arnold, Elmer, and Dodson, J. Amer. Chem. Soc., 1950, 72, 4359.
 <sup>4</sup> Westheimer, Proc. Chem. Soc., 1963, 253, and references cited therein.

<sup>&</sup>lt;sup>5</sup> Linstead, J., 1930, 1603.

<sup>&</sup>lt;sup>6</sup> Foster, Cope, and Daniels, J. Amer. Chem. Soc., 1947, 69, 1893. 6 K

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is of interest in this connection that a crude rate study showed tiglic acid to decarboxylate more slowly than 2-methylbut-2-enoic acid.<sup>7</sup> It seems therefore that, at least in this case, the isomerization is slower than the decarboxylation.

(i) The production of terminal olefins by thermal decarboxylation. When acids 7 and 11 (Table) were decarboxylated in evacuated sealed tubes, the resultant olefin was contaminated (up to 20%) with isomerized products. Such isomerization has previously been reported.<sup>8</sup> When the experiments were repeated under conditions where the olefin was

Products and yields of thermal decarboxylations.

			Yield (%)	
No.	Acid *	Olefin	Olefin	$CO_2$
1	CH2:CH·CH2·CO2H	Prop-1-ene	61	90
<b>2</b>	CH <sub>2</sub> ·CH·CH(CH <sub>3</sub> )·CO <sub>2</sub> H	trans-But-2-ene	82	85
3	$CH_3 \cdot CH \cdot C(CH_3) \cdot CO_2 H$ (Tiglic acid)	trans-But-2-ene	75	99
4	trans-CH <sub>a</sub> ·CH:C(C <sub>2</sub> H <sub>5</sub> )·CO <sub>2</sub> H	trans-Pent-2-ene	75	85
<b>5</b>	CH <sub>2</sub> :CH·C(CH <sub>3</sub> ) <sub>2</sub> ·CO <sub>2</sub> H	2-Methylbut-2-ene	79	92
6	$CH_2:C(CH_3) \cdot C(CH_3)_2 \cdot CO_2H$	2,3-Dimethylbut-2-ene <sup>7</sup>	67	85
7	CH <sub>3</sub> ·CH:CH·CH <sub>2</sub> ·CO <sub>2</sub> H	But-1-ene	72	95
8	$CH_3 \cdot CH_2 \cdot CH \cdot C(CH_3) \cdot CO_2 H$	trans-Pent-2-ene †	57	60
9	trans-CH <sub>3</sub> ·CH:CH·C(CH <sub>3</sub> ) <sub>2</sub> ·CO <sub>2</sub> H	2-Methylpent-2-ene	86	98
10	trans-C <sub>6</sub> H <sub>5</sub> ·CH:CH·C(CH <sub>3</sub> ) <sub>2</sub> ·CO <sub>2</sub> H	2-Methyl-4-phenylbut-2-ene		99
11	CH <sub>3</sub> ·CH:C(CH <sub>3</sub> )·CH <sub>2</sub> ·CO <sub>2</sub> H	2-Methylbut-1-ene	<b>65</b>	85
12	CH <sub>3</sub> ·[CH <sub>2</sub> ] <sub>5</sub> ·CH.CH.C(CH <sub>3</sub> ) <sub>2</sub> ·CO <sub>2</sub> H	2-Methyldec-2-ene		95

\* The stereochemistry of the double bond is indicated where known. † Decarboxylation incomplete after 8 hr.

removed, as soon as produced, from contact with the parent acid, the pure terminal olefins were produced.

(ii) The stereochemistry of decarboxylation. Since a trans-olefin is normally more stable than its cis-isomer, the observation of trans-olefins as the sole products of decarboxylation is not significant unless it can be shown that they are also the first products of decarboxylation. This was demonstrated by decarboxylating the acids 2, 3, 4, and 8 under conditions which do not lead to the isomerization of terminal olefins. Pure trans-olefins resulted.

(iii) The fate of the carboxyl hydrogen atom. Deuterium labelling was used to examine the behaviour of the carboxyl hydrogen atom. Initial experiments were performed on 2-methylbut-2-enoic acid, but it was soon apparent that the label became scrambled prior to decarboxylation. In a second experiment, the same acid was four times heated to  $150^{\circ}$  in a sealed tube with a twenty-fold excess of deuterium oxide. Under these conditions it was hoped that the hydrogen on the  $\alpha$ -carbon atom would exchange, as would its vinylogues on the  $\gamma$ -carbon atom. There should result a mixture of CD<sub>2</sub>:CH·CD(CH<sub>3</sub>)·CO<sub>2</sub>D and CD<sub>3</sub>·CH:C(CH<sub>3</sub>)·CO<sub>2</sub>D, which, on decarboxylation, should give rise only to CD<sub>3</sub>·CH:CD·CH<sub>3</sub>, readily identifiable by nuclear magnetic resonance (n.m.r.) spectroscopy. In practice it was found that before the protons on the  $\alpha$ - and  $\gamma$ -carbon atoms had totally exchanged, 30-40% of deuterium had appeared on the  $\beta$ -carbon atom.

In order to prevent scrambling of the label from the carboxyl group an acid with no  $\alpha$ -hydrogen atom and incapable of  $\beta\gamma$ - to  $\alpha\beta$ -double-bond migration was chosen. The simplest such acid, 2,2-dimethylbut-3-enoic acid (5), was not selected since, contrary to an earlier report,<sup>3</sup> acid recovered from partial decarboxylation did not appear to be entirely unchanged. Further, the resultant olefin would contain a maximum of one deuterium atom in one of three methyl groups, and the methyl proton area would drop only from nine units to eight. Small deviations from expected behaviour would not easily be detected in so limited an area change. A more suitable acid was 2,2-dimethylpent-3-enoic acid (9) which could be recovered unchanged after partial decarboxylation. The pro-

<sup>&</sup>lt;sup>7</sup> Hotter, Project Thesis, Loughborough, 1963.

<sup>&</sup>lt;sup>8</sup> Arnold and Danzig, J. Amer. Chem. Soc., 1957, 79, 892.

duct of decarboxylation of the carboxyl-deuterated form of this acid is expected to be  $CH_3 \cdot CHD \cdot CH \cdot C(CH_3)_2$  and the main features of the experimentally determined n.m.r. spectrum were in complete accord with such a structure. The area of the CHD group was half the corresponding area of the non-deuterated olefin and the triplets associated with the 3-methine and 5-methyl protons of the latter became doublets in the deuterated olefin. Approximately 15% of the 5-methyl group remained as a triplet, however, indicating that either there is a small amount of exchange during decarboxylation, or there is a second minor pathway to decarboxylation. Nevertheless, *ca.* 85% of the label appears in the expected position.

(iv) *Kinetics*. None of the acids listed in the Table was sufficiently involatile to permit the kinetics of the reaction to be measured in an open system. Accordingly the rate of decarboxylation of 2,2-dimethyl-4-phenylbut-3-enoic acid (10) was measured as a melt in sealed tubes. The reaction was followed by measuring the carbon dioxide produced, and a good first-order plot was obtained up to 70% reaction. Three determinations at 259° gave  $10^{6}k = 7.81 \pm 0.03$  sec.<sup>-1</sup>.

## EXPERIMENTAL

The unsaturated acids were synthesized by standard literature methods and were carefully purified by distillation or crystallization.

Decarboxylations were performed by refluxing a mixture of the acid (1 g.) and recrystallized phenanthrene (10 g.) under a stream of dry nitrogen in a 25 ml. flask attached to a steam-heated reflux condenser (8 hr.). In this way the olefin was swept out as soon as formed and the phenanthrene and acid were returned to the flask. The olefin was collected in a trap cooled in ice or acetone and solid carbon dioxide, and the carbon dioxide was then absorbed with soda asbestos. The olefins were handled by normal vacuum-line methods, and were identified by their infrared  $^{9}$  and n.m.r. spectra. The carbon dioxide was estimated by weight. Earlier experiments performed in evacuated sealed tubes at  $325^{\circ}$  gave partially isomerized olefins.

The carboxyl group of the acids was labelled with deuterium by the previously published method.<sup>10</sup> Under these conditions, mass-spectral analysis indicated less than 0.1% double-labelling of 2-methylbut-3-enoic acid, whilst the n.m.r. spectrum showed the carboxyl proton to be completely exchanged. When 2-methylbut-3-enoic acid was so labelled and heated to 300° for 0.5 hr., the acid recovered on cooling contained only 22% of the original deuterium in the carboxyl group.

The kinetics of decarboxylation of 2,2-dimethyl-4-phenylbut-3-enoic acid were measured on the molten acid. Standard amounts of acid were transferred as a chloroform solution to tubes equipped with a break-seal, and the chloroform was removed. The tubes were sealed under vacuum and the kinetic run was performed. Each tube was cooled to  $-80^{\circ}$ , the break-seal was opened, and the carbon dioxide measured in a vacuum system.

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<sup>9</sup> American Petroleum Institute, Project 44, Carnegie Institute of Technology, Pittsburgh 13, Pa.
 <sup>10</sup> Bigley, J., 1964, 876.