Evidence of this was given by the hydrogenation of octadecenoic acids in which the double bond was located at different positions along the chain.[20] It was found[20] that the highest rate of hydrogenation occurred with the bond in the 9-position and the lowest rate with the bond in the 2-position. This is in accord with the observations of Ponzio and Gastaldi[21] who obtained the same relative rates for the absorption of halogens by the same group of acids. Although the rate of reaction was not determined for 10-octadecenoic acid, it would be expected on the basis of these results that this acid would undergo hydrogenation more readily than oleic or elaidic acid. Thus, in any catalytic reduction where 8-, 9- and 10-octadecenoic acids are produced (or are present) the 10-acid

(20) G. V. Pigulevskii and P. A. Antamonox, *J. Gen. Chem. (USSR)*, **12**, 510 (1942).

(21) G. Ponzio and C. Gastaldi, *Gazz. chim. ital.*, **42**, II, 93 (1912).

should disappear most readily and the 8-acid least. This was borne out to some extent in this particular hydrogenation study.

The experimental conditions contributing to the production of the relatively large amounts of iso-oleic acids were probably the low activity and the character of the Raney nickel catalyst and also the very limited agitation employed.

### Summary

Triolein was partially hydrogenated under conditions which gave rise to a relatively large amount of iso-oleic acids. *trans*-8-Octadecenoic and elaidic acids were isolated from the reaction products and their identity proven chemically and physically.

Data are also reported for a new acid, 8,9-dihydroxystearic acid, m. p. 128°, obtained by the partial oxidation of *trans*-8-octadecenoic acid.

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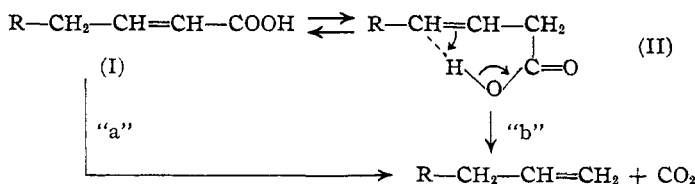## Thermal Decarboxylation of Unsaturated Acids

BY RICHARD T. ARNOLD, OTTO C. ELMER[1] AND R. M. DODSON

Carboxylic acids (and their derivatives) lose carbon dioxide under a variety of experimental conditions and undoubtedly by many different mechanisms. Several aspects of the decarboxylation reaction have been summarized[2] and the role of acid catalysis in the decomposition of cinnamic acid (and related compounds) has been clearly demonstrated.[3,2]

An elegant study by Linstead and co-workers[4,5,6] has established the fact that through a simple prototropic shift $\alpha,\beta$- and $\beta,\gamma$-unsaturated acids will frequently enter into mobile equilibrium. Linstead's work indicates that thermal decarboxylation of certain $\alpha,\beta$-unsaturated acids may actually proceed *via* the $\beta,\gamma$-isomer as an intermediate.
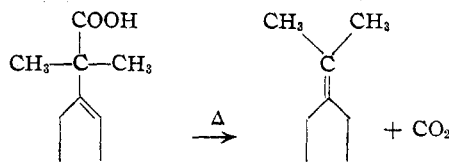
It is an experimental fact that the olefins resulting from pyrolysis of simple $\alpha,\beta$-unsaturated acids are homogeneous and contain terminal unsaturation.

Two different mechanisms ("a" and "b") leading to the same olefin are formulated here. Mechanism "a" is essentially that proposed for the cinnamic acid decompositions.[3] Mechanism "b" assumes that (I) first isomerizes to the $\beta,\gamma$ isomer (II) which then decarboxylates



through a cyclic transition complex as proposed for the thermal decomposition of $\beta$-keto acids.[7,8,9] It is the purpose of this paper to point out the fact that $\beta,\gamma$-unsaturated acids are thermally unstable and probably decarboxylate preferentially when in mobile thermodynamic equilibrium with the corresponding $\alpha,\beta$-isomers.

Careful examination of the older literature[10,11] reveals several cases pointing to the thermal instability of $\beta,\gamma$-unsaturated acids. It is signifi-



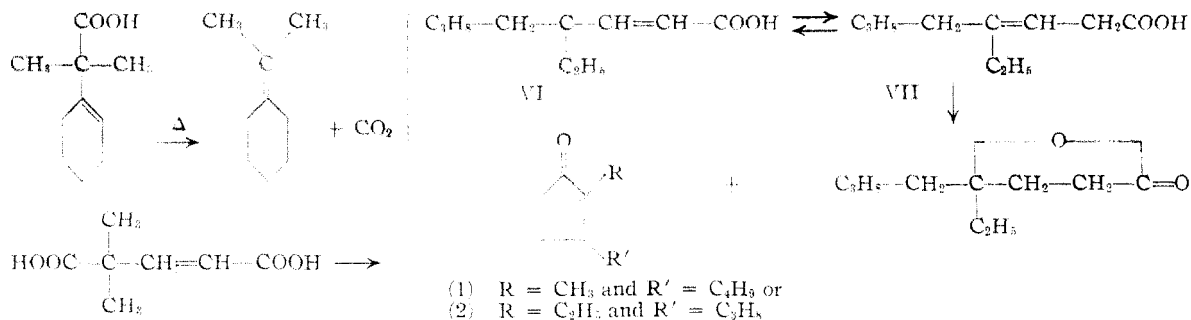(1) From the Ph.D. thesis of Otto C. Elmer presented to the Graduate Faculty in October, 1948.

(2) Schenkel and Schenkel-Rudin, *Helv. Chim. Acta*, **31**, 514 (1948).

(3) Johnson and Heinz, THIS JOURNAL, **71**, 2913 (1949).

(4) Kon and Linstead, *J. Chem. Soc.*, **127**, 616 (1925).

(5) Eccott and Linstead, *ibid.*, 2153 (1929).

(6) Linstead, *ibid.*, 1603 (1930).

(7) Westheimer and Jones, THIS JOURNAL, **63**, 3283 (1941).

(8) King, *ibid.*, **69**, 2738 (1947).

(9) Mechanism "b" as a possible route for the thermal decarboxylation of $\alpha,\beta$-unsaturated acids was first proposed by one of us (R. T. A.) in a lecture before the Organic Division of the American Chemical Society in Boston, June, 1947. Dr. T. G. Halsall (Manchester, England) has just notified us (March 14, 1950) of his observations dealing with the thermal instability of $\beta,\gamma$-unsaturated acids in the terpene series.

(10) Wallach, *Ann.*, **353**, 304 (1907); **360**, 68 (1908).

(11) Blaise and Courtot, *Bull. soc. chim.*, [3] **35**, 151 (1906).

(1)  R = CH₃ and R' = C₄H₉ or
(2)  R = C₂H₅ and R' = C₃H₇

cant that in each of the above cases, thermal decarboxylation is accompanied by a shift of the carbon–carbon double bond as required by mechanism "b."
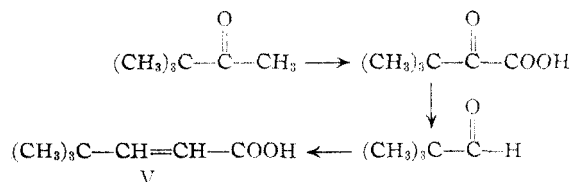
We have examined the pyrolysis of 2,2-dimethylbuten-3-oic acid (III) and have identified 2-methylbuten-2 (IV) as the sole olefinic product.



Since in the above examples, rearrangement of the $\beta,\gamma$-acid into its corresponding $\alpha,\beta$ isomer is impossible (in the absence of a carbon skeletal rearrangement), it was decided to prepare and study an $\alpha,\beta$-unsaturated acid which could not isomerize to the $\beta,\gamma$ structure by simple prototropic shift. 4,4-Dimethylpenten-2-oic acid (V) was synthesized as indicated. This acid (prob-
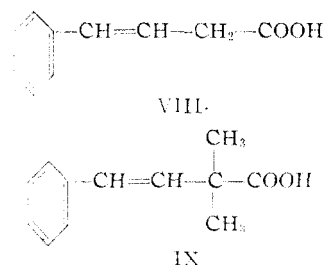


ably the *trans* modification, m. p. 61–62°) when heated at 300° for two hours remained essentially unchanged.

Alkyl groups, particularly when located at the $\gamma$-carbon atom, have a marked effect on the rate of elimination of carbon dioxide from $\alpha,\beta$- or $\beta,\gamma$-unsaturated acids. When 4-ethylocten-2-oic acid (VI) was heated at 200–250°, a neutral fraction (containing lactone and $\alpha,\beta$-unsaturated cyclic ketone) was isolated as major product. The residual undecomposed acid was isomeric with the starting material and presumed to be largely $\beta,\gamma$ isomer (VII). This formation of lactone[12,18] and cyclic ketone[14,15] was anticipated and is understandable on the following basis.

(12)  Willstätter and Hatt, *Ann.*, **418**, 148 (1919).
(13)  Johnson and Hunt, THIS JOURNAL, **72**, 935 (1950).
(14)  Frank, Arvan, Richter and Vanneman, *ibid.*, **66**, 4 (1944).
(15)  Frank, Armstrong, Kwiatek and Price, *ibid.*, **70**, 1379 (1948).

Linstead[6] found that styrylacetic acid (VIII) is unusually stable toward heat. We have found the same to be true of $\alpha,\alpha$-dimethylstyrylacetic acid (IX).



Since decarboxylation (*via* route "b" above) in these cases, of necessity, leads to destruction of the conjugated system, the observed thermal stability is not too surprising.

Preliminary rate studies (in solution) on the decarboxylation of $\alpha,\beta$-unsaturated acids which readily isomerize (thermally) to their $\beta,\gamma$ forms indicate first order kinetics in agreement with the above considerations.

## Experimental

**2,2-Dimethylbuten-3-oic Acid (III).**—This substance was prepared from acetaldehyde, ethyl $\alpha$-bromoisobutyrate, and zinc to give ethyl $\beta$-hydroxy-$\alpha,\alpha$-dimethylbutyrate (67% yield) following the method of Blaise and Courtot.[11] Dehydration (with $P_2O_5$) and saponification gave the desired 2,2-dimethylbuten-3-oic acid; b. p. 85–87° (5 mm.). Neut. equiv. calcd.: 114. Found: 113.

**Pyrolysis of 2,2-Dimethylbuten-3-oic Acid (III).**—A sample of the acid (3.9 g.) was sealed into a short Carius tube and left overnight at a temperature of 260°. The tube was cooled to −35°, opened, and the olefin distilled; b. p. 40°; $n^{20}D$ 1.3870. Comparison with the following data serves to establish the identity as 2-methylbutene-2.

| Substance | $nD$ | B. p., °C. |
|---|---|---|
| 2-Methylbutene-2 | 1.3878/20° | 38.4 |
| 3-Methylbutene-1 | 1.3675/15° | 20.1 |
| 2-Methylbutene-1 | 1.3777/20° | 31.05 |

In a second experiment 2,2-dimethylbuten-3-oic acid (0.135 g.) was heated in a sealed tube at 250° for five hours. Titration with standard alkali showed only 25% of the unsaturated acid remaining.

**4,4-Dimethylpenten-2-oic Acid.**—Pinacolone was converted into pivalaldehyde by the procedure of Richards[16] and Glückmann.[17]

(16)  Richards, *Ann. chim. phys.*, [8] **21**, 360 (1910).
(17)  Glückmann, *Monatsh.*, **10**, 770 (1889).

Pivalaldehyde (7.6 g.), malonic acid (10 g.), pyridine (35 ml.) and piperidine (3 ml.) were refluxed together for twelve hours. The cooled solution was poured onto ice and concentrated hydrochloric acid and the whole extracted with ether. After drying the ether solution with sodium sulfate, evaporation of the solvent left a pale yellow liquid (2 g.). Distillation in a "sausage" flask under vacuum gave a white solid which after recrystallization from aqueous ethanol melted at 61–62°.

*Anal.* Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44; neut. equiv., 128. Found: C, 65.56; H, 9.41; neut. equiv., 126.

**Attempted Pyrolysis of 4,4-Dimethylpenten-2-oic Acid.** —In a preliminary test, a small sample of the acid was heated in a sealed tube at 240° for thirty minutes. After cooling, the solidified sample proved to be identical with the starting acid. In a second run, a sample of acid was sealed in Pyrex tubing and heated at 300° for five hours. Upon cooling, the total contents of the tube was soluble in sodium hydroxide and the starting carboxylic acid had undergone no change.

**α,α-Dimethylstyrylacetic Acid.**—Several attempts to prepare this compound by use of the Reformatsky reaction failed. Ethyl styrylacetate (27.3 g.) was added to lithium amide (3.4 g.) powder in dry ether (150 ml.). After thirty minutes, methyl iodide (30 g.) dissolved in ether (50 ml.) was added and the solution was refluxed for fifteen hours. Decomposition with water, separation of the ether layer and distillation of the latter gave a liquid; b. p. 142° (10 mm.). This material was not homogeneous and a portion (8 g.) was remethylated using the conditions described above. After decomposition of the reaction mixture with water, evaporation of the ether layer gave a white solid; 2.5 g.; m. p. 131–132°. This material gave a positive test for nitrogen and analyzed for α,α-dimethylstyrylacetamide.

*Anal.* Calcd. for $C_{12}H_{15}ON$: C, 76.15; H, 7.99. Found: C, 76.15; H, 7.92.

Ozonolysis of the above compound (in ethyl bromide solution) yielded benzaldehyde proving that alkylation occurred at the alpha position. Hydrolysis of the above amide gave a carboxylic acid (presumably α,α-dimethylstyrylacetic acid); m. p. 110–111°.

*Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.67; H, 7.73.

**Pyrolysis of Styrylacetic Acids.**—At 240° for extended periods of time a slight change of color occurred. At 300° both acids showed signs of change but no olefin or carbon dioxide could be detected.

**4-Ethylocten-2-oic Acid (VI).**—Redistilled 2-ethylhexanol ("Octaldehyde") (200 g.) was mixed with malonic acid (164 g.), dry pyridine (200 g.) and a little piperidine.

This mixture was heated at 70–80° (steam-bath) for two hours, cooled, made acid to congo red and extracted with ether. Direct distillation returned much of the starting aldehyde and gave 4-ethylocten-2-oic acid; yield 28%; b. p. 124° (4 mm.).

*Anal.* Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66; neut. equiv., 170. Found: C, 70.49; H, 10.50; neut. equiv., 171.6.

An anilide of the above acid melted at 59–60°.

*Anal.* Calcd. for $C_{16}H_{23}ON$: C, 78.32; H, 9.45. Found: C, 78.58; H, 9.74.

**Pyrolysis of 4-Ethylocten-2-oic Acid.**—The above acid was heated for thirty minutes at a temperature of 290°. A slow stream of nitrogen entrapped a small quantity of carbon dioxide which was collected as barium carbonate. Extraction with dilute alkali gave a neutral and acidic fraction. Distillation of the neutral portion gave fractions boiling at 96° (3 mm.) and 106° (3 mm.). These could not be separated completely by fractionation with the quantity of material available.

The first fraction was an α,β-unsaturated ketone. It absorbed markedly at 2350 Å. and formed a 2,4-dinitrophenylhydrazone; m. p. 108–110°.

*Anal.* Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07. Found: C, 57.47; H, 5.92.

No absorption down to 2200 Å. was found for the higher boiling neutral fraction. Its analysis and general properties indicate the γ-lactone structure.

*Anal.* Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 71.45; H, 10.98.

The acid residue is isomeric with the starting acid (*i.e.*, neutral equivalent 174; calculated 170). In contrast to the starting material, this acid rapidly decolorizes bromine and does not show the absorption spectra characteristic of α,β-unsaturation in the ultraviolet region. It is undoubtedly the β,γ-isomer.

## Summary

1. A new mechanism has been proposed for the thermal decarboxylation of certain α,β-unsaturated acids.

2. This mechanism assumes that the α,β-unsaturated acid isomerizes first to the β,γ structure which eliminates carbon dioxide through a cyclic transition state in a manner similar to that for the decomposition of β-keto acids.

3. Several examples are cited.