kept cold by an ice-bath. When the color of chromyl chloride was discharged the flask had gained 23 g. in weight, corresponding to 0.55 mole of propylene absorbed. The solid was filtered, washed, and hydrolyzed in cold sodium bisulfite solution. The aqueous solution was saturated with salt, extracted with ether, and the latter solution dried over sodium sulfate. Distillation gave 22.4 g. (43%) of 2-chloro-1-propanol, b. p. 121–124° (613 mm.), n^{20}_D 1.4377, m. p. of 3,5-dinitrobenzoate 76.5–77.5°.[28] The melting point of the dinitrobenzoate was not depressed when mixed with that of an authentic sample of 2-chloro-1-propanol.[29] But when mixed with the 3,5-dinitrobenzoate (m. p. 76–76.5°) of 1-chloro-2-propanol,[30] the melting point was 59–65°.

2-Chloro-1-butanol.—Phillips "Pure Grade" 1-butene was treated with chromyl chloride in a manner similar to the reaction of propylene with chromyl chloride. The product boiling at 49–53° (13 mm.) amounted to 49% of theory, n^{20}_D 1.4428.[31] The 3,5-dinitrobenzoate, after four recrystallizations from aqueous alcohol, melted at 74–76°.

Anal. Calcd. for $C_{11}H_{11}O_6N_2Cl$: N, 9.26. Found: N, 9.22.

Five grams of the 2-chloro-1-butanol was warmed with concentrated nitric acid. After neutralization with sodium bicarbonate, acidification to a *p*H of 4 with sulfuric acid, extraction with ether and distillation, 1.5 g. of an acid was obtained, boiling at 189° (627 mm.). The acid contained chlorine and had a neutral equivalent of 122; the neutral equivalent calculated for α-chlorobutyric acid[32] is 122.5.

The acetate was prepared by refluxing 9 g. of 2-chloro-1-butanol with 20 g. of acetic anhydride for three hours. Water was added, and the immiscible acetate was separated, washed with sodium bicarbonate, dried over sodium sulfate, and distilled, giving 5.5 g. of the acetate, b. p. 158–162° (630 mm.); n^{25}_D 1.4255; d^{25}_4 1.0601; M_D, calcd., 36.43; found, 36.36.

2-Chloro-1-pentanol.—By treating 1-pentene with chromyl chloride in a manner similar to those with propylene and 1-butene, a 43% yield of 2-chloro-1-pentanol was obtained, b. p. 59–64° (13 mm.), n^{20}_D 1.4457.

The 3,5-dinitrobenzoate was prepared; after three recrystallizations from 95% ethanol it melted at 69.5–71°.

Anal. Calcd. for $C_{12}H_{13}O_6N_2Cl$: N, 8.85. Found: N, 8.83.

Twenty-five grams of 2-chloro-1-pentanol was stirred with a solution of 180 g. of potassium dichromate in 150 ml. of concd. sulfuric acid and 500 ml. of water at room temperature for twelve hours. Extraction with ether and distillation gave 7.6 g. of α-chlorovaleric acid,[33] b. p. 111–121° (15 mm.); n^{11}_D 1.4497; n^{23}_D 1.4441; d^{23}_4 1.119; neut. equiv., calcd. 136.5, found, 141; M_D calcd., 31.69, found, 32.43.

Anal. Calcd. for $C_5H_9O_2Cl$: Cl, 25.96. Found: Cl, 25.94.

2-Chloro-1-hexanol.—This compound was prepared from 1-hexene as above. Forty-two grams (36%) of product was obtained from 84 g. of 1-hexene, n^{20}_D 1.4486. Attempts to prepare the 3,5-dinitrobenzoate were unsuccessful. Oxidation by sulfuric acid–potassium dichromate mixture produced α-chlorocaproic acid,[34] b. p. 125° (15 mm.); n^{23}_D 1.4428; d^{23}_4 1.091; neut. equiv., calcd., 150.5; found, 154; M_D, calcd., 36.31; found, 36.58.

Acknowledgment.—The authors are grateful to Julius Hyman and Company, Inc., Denver, Colorado, for generous financial support of this work.

Summary

A novel reaction has been found in which chromyl chloride reacts with olefins to give chlorohydrins. Cyclohexene has been converted to *trans*-2-chlorocyclohexanol in fair yields, and aliphatic olefins of the type $RCH{=}CH_2$ have been converted to β-chloro primary alcohols in 35–50% yields.

A possible mechanism is proposed for the reaction, consistent with the products observed and the relative reactivities of the olefins studied.

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[28] Gayler and Waddle, This Journal, **63**, 3359 (1941).

[29] Dewael, *Bull. soc. chim. Belg.*, **33**, 504 (1924).

[30] Henry, *Ber.*, **7**, 414 (1874); *Rec. trav. chim.*, **22**, 324 (1903).

[31] Waddle and Adkins, This Journal, **61**, 3361 (1939).

[32] De Boosere, *Bull. soc. chim. Belg.*, **32**, 44 (1923).

[33] Servais, *Rec. trav. chim.*, **20**, 45 (1901).

[34] Guest, This Journal, **69**, 300 (1947).

BOULDER, COLORADO RECEIVED MARCH 10, 1950

[CONTRIBUTION NO. 765 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Partial Hydrogenation of Triolein

BY JAMES H. BENEDICT[1,2] AND B. F. DAUBERT

Introduction

Although it is known that the partial hydrogenation of oleic acid or its esters results in the formation of iso-oleic acids in addition to stearic acid, there is not complete agreement as to which isomers are produced. Moore[3] in 1919 partially hydrogenated ethyl oleate using palladium and nickel catalysts at 140 and 240°. Although he made no separation of his reaction products, Moore[3] concluded that the iso-oleic acids produced during these hydrogenations consisted of a mixture of 9-, 10- and 11-*trans*-octadecenoic acids.

Hilditch and Vidyarthi[4] hydrogenated methyl oleate using a nickel catalyst and then separated the solid fatty acids from the reaction products by the Twitchell lead salt procedure. On the basis of a potassium permanganate oxidation, they concluded that the hydrogenation produced 8-, 9- and 10-octadecenoic acids.

Since natural oils are composed of triglycerides it seemed desirable to study the course of the hydrogenation reaction for the simple triglyceride, triolein. While conducting this investigation a sample of triolein was hydrogenated in such a manner that a relatively large quantity of iso-oleic acids was produced.

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[1] Procter and Gamble Company Fellow.

[2] Procter and Gamble Company, Cincinnati 17, Ohio.

[3] C. W. Moore, *J. Soc. Chem. Ind.*, **38**, 320T (1919).

[4] T. P. Hilditch and N. L. Vidyarthi, *Proc. Roy. Soc. (London)*, **A122**, 552 (1929).

It is the purpose of this communication to report the operating conditions used for this particular hydrogenation, and the details for the isolation and characterization of two of the iso-oleic acids that were produced.

Experimental

The **Raney nickel catalyst** was prepared by a slight modification of the method described in "Organic Syntheses."[5]

The **triolein** was isolated from virgin-grade olive oil. In order to reduce the amount of polyunsaturated components in the oil, olive oil was hydrogenated at room temperature and 100 pounds gage pressure with palladium black as the catalyst for only fifteen minutes. After removing this catalyst by suction filtration, the oil was dissolved in acetone, cooled to −15°, equilibrated, and the precipitate of saturated glycerides removed by filtration. The filtrate was then cooled to −45°, equilibrated, and the white precipitate of triolein filtered off. When the triolein had warmed to room temperature, the excess solvent was removed with gentle heating under reduced pressure; I. V., 84.0 (calcd. 86.0); free fatty acid less than 0.01 per cent.; m. p. −6°. An infrared spectrogram of the triolein indicated the absence of *trans* isomers.

Hydrogenation.—Triolein (90 g.) was partially hydrogenated at 180–200°, 70 pounds gage pressure, with 0.05% Raney nickel catalyst and limited stirring in a Parr medium pressure hydrogenation unit. After a three hour reaction period with a 5 pound gage pressure drop, the unit was cooled to room temperature and the sample removed. A relatively large amount of solids was present in the hydrogenated oil. The hydrogenated oil was warmed, suction filtered through very fine filter paper (Schleicher and Schuell, No. 576). Iodine value was 74.9; melting began at about 30° and was complete at 48°.

Isolation of the Iso-oleic Acids.—The quantitative estimation of the iso-oleic acids present in the hydrogenated sample was made by the lead salt–ethanol separation.[6] The sample was found to contain 35.3% iso-oleic acids.

In order to isolate some of the iso-oleic acids that were produced during hydrogenation the mixed fatty acids (21.2 g.) arising from the saponification of the 26.8 g. of hydrogenated triolein were subjected to a lead salt–ethanol separation.[6] The yield was 10.8 g. of solid acids.

The solid acids (4.18 g.) were dissolved in 10 ml. of methanol. Separately, mercuric acetate (4.5 g.) was heated in glacial acetic acid (9 ml.) and methanol (10 ml.) and then added slowly to the solution of the solid acids with stirring. The mixture was allowed to cool to room temperature overnight. This precipitate was filtered (I), washed three times with 10-ml. portions of methanol and suction dried. The insoluble soaps were heated in 50 ml. of ethyl ether, and concentrated hydrochloric acid (15 ml.) was added to free the fatty acids. The ether solution was washed five times with water and dried over anhydrous sodium sulfate. After removing the ether, the product melted at 59.0–60.0°; yield, 1.0 g. Fractional crystallization from petroleum ether yielded a small amount of stearic acid, m. p. 68.5°.

The filtrate from the above mercury soap filtration (I) was adjusted to a volume of 25 ml. by the addition of methanol, and allowed to stand at 5° overnight. The small amount of precipitate was filtered (IA), washed, and dried. The fatty acids were freed in the same manner as described above; yield, 0.8 g.; m. p. 54.0–55.5°. These acids were taken up in petroleum ether (100 ml.), warmed and the slight precipitate formed upon cooling was removed. The solution was cooled to 5°, filtered and dried. The acid was reconverted to the mercury soaps, crystallized from 20 ml. of solution, filtered (II), and the acids recovered as before. The product melted at 53.0–54.0°. This material was further purified by recrystallization from petroleum ether and ethyl ether; yield, 0.6 g., m. p. 52.5–53.5°.

The filtrate from the second mercury soap filtration (IA) was freed of methanol and the soaps, dissolved in ethyl ether, converted to the free fatty acids by the aforementioned method. The product melted at 26–36°; yield, 2.4 g. Upon crystallizing these acids from ethyl ether a solid acid, melting at 44.5–45.5°, and a liquid acid, melting at 10°, were obtained.

The filtrate from the latter mercury soap separation (II) was evaporated to dryness and the small amount of fatty acids recovered; m. p. 45–46°. This acid (m. p. 45–46°) was combined with the above solid acid (m. p. 44.5–45.5°) and recrystallized several times from ethyl ether and petroleum ether to yield an acid with a melting point of 44.5–45.6°; yield 1.5 g.

The remaining 5.5 g. of the solid acid from the lead salt separation was subjected to exactly the same separation as described above. The respective acids from the two separations were combined and recrystallized from ethyl ether. These three acids were later identified as *trans*-8-octadecenoic acid, m. p. 52.4–53.4°, I. V. 87.5 (calcd. 89.9), yield 1.1 g.; *trans*-9-octadecenoic acid, m. p. 44.8–45.5°, I. V. 88.3 (calcd. 89.9), yield 3.9 g.; *cis*-9-octadecenoic acid, m. p. 10–11°, I. V. 89.2 (calcd. 89.9), yield 1.8 g.

Identification of *trans*-8-Octadecenoic Acids.—The 8-octadecenoic acid (1.0 g.) was converted to dihydroxystearic acid by the peracetic acid oxidation according to the method of Swern, *et al.*[7] The yield of 8,9-dihydroxystearic acid after recrystallizing from petroleum ether (b. p. 35–45°) was 0.98 g. (89%); m. p. 127–128°; iodine value 0.9 (calcd. 0.0).

Anal.[8] Calcd. for $C_{18}H_{36}O_4$: C, 68.31; H, 11.46. Found: C, 68.13, 68.43; H, 11.46, 11.31.

The 8,9-dihydroxystearic acid was oxidatively degraded with lead tetraacetate[9] by dissolving the acid (0.9 g.) in 10 ml. of anhydrous acetic acid and then adding 10 g. of lead tetraacetate.[10] After shaking for one-half hour at room temperature and five minutes at 45°, the mixture was cooled, diluted with 10 ml. of water, sufficient 3 *N* hydrochloric acid added to dissolve the precipitated lead oxide, and the solution thoroughly shaken out with ethyl ether. The ether solution was thoroughly extracted with 5% sodium carbonate solution, and washed with water until neutral to litmus. The ether solution was dried over anhydrous sodium sulfate, and the ether removed by evaporation under reduced pressure. The residue of capric aldehyde (0.32 g.) was distilled in a microdistillation apparatus under an atmosphere of nitrogen. The fraction boiling at 201–206° was collected (lit.[11] b. p., 208–209°). The identity of this compound was confirmed by the preparation of the oxime,[12] m. p. 67–68° (lit.[11] m. p. 69.0°).

Anal. Calcd. for $C_{10}H_{21}ON$: C, 70.12; H, 12.36; N, 8.17. Found: C, 70.04; H, 12.08; N, 7.86, 7.77.

The remaining aldehyde was oxidized to capric acid by bubbling oxygen through the warmed oil and recrystallizing from acetone. The acid, m. p. 29–30° (lit.[13] m. p., 31.3°), was converted to the *p*-bromophenacyl ester, m. p. 66–67° (lit.[14] m. p., 67.0).

Anal. Calcd. for $C_{18}H_{25}O_3Br$: C, 58.54; H, 6.82; Br, 21.64. Found: C, 58.72; H, 6.82; Br, 21.48.

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[5] *Organic Syntheses*, **21**, 15 (1941).

[6] V. C. Mehlenbacker, Editor, "Official and Tentative Methods," Am. Oil Chemists' Society, Chicago, 1946.

[7] D. Swern, G. H. Billen, T. W. Findley and J. T. Scanlan, THIS JOURNAL, **67**, 1786 (1945).

[8] The microanalyses were performed by Mr. George Stragand, University of Pittsburgh.

[9] J. T. Scanlan and D. Swern, *ibid.*, **62**, 2305 (1940).

[10] R. E. Oesper and C. L. Deasy, *ibid.*, **61**, 972 (1939).

[11] A. K. Ralston, "Fatty Acids and Their Derivatives," John Wiley, New York, 1948, p. 821.

[12] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y. 1948, p. 202.

[13] Daffet, *Bull. Soc. Chim. Belg.*, **40**, 385 (1931).

[14] C. G. Moses and E. E. Reid, THIS JOURNAL, **54**, 2101 (1932).

The alkaline extracts were acidified, extracted with ether, washed and concentrated after drying. The aldehydoacid was separated from the concentrate by the addition of a saturated sodium bisulfite solution. The free acid obtained upon acidification of the sodium bisulfite addition product was oxidized to the dibasic acid with alkaline permanganate. The suberic acid (0.24 g.) after three recrystallizations from ethyl ether melted at 140–141° (lit.[15] m. p. 140°); neutral equivalent, 87.4 (calcd. 87.1); it was identified as the *p*-bromophenacyl ester, m. p. 144.0° (lit.[16] 144.2°).

Identification of Elaidic Acid.—The isolated *trans*-9-octadecenoic (elaidic) acid was oxidized with peracetic acid as above to 9,10-dihydroxystearic acid, m. p. 131° (lit.[7] m. p. 131°). The dihydroxystearic acid was cleaved with lead tetraacetate[9] in the same manner as before. The aldehyde, b. p. 181–185° (lit.[11] 185°), obtained thereby was converted to the oxime,[12] m. p. 63° (lit.[11] m. p. 64°). *Anal.* Calcd. for $C_9H_{19}ON$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.80; H, 11.95; N, 9.13. Some of the aldehyde was oxidized to pelargonic acid, m. p. 12° (lit.[13] m. p., 12.3°), which was identified as the *p*-bromophenacyl ester, m. p. 67° (lit.[14] m. p., 68.5°). The aldehydoacid fraction was oxidized with alkaline permanganate. The azelaic acid was purified by a series of extractions between ethyl ether and water, and recrystallized from water; m. p. 106° (lit.[15] m. p., 107°); neut. equiv. 93.9 (calcd. 94.1). The acid was converted to the *p*-bromophenacyl ester, m. p. 130.5° (lit.[16] m. p., 130.6°). *Anal.* Calcd. for $C_{25}H_{26}O_6Br_2$: C, 51.56; H, 4.50; Br, 27.45. Found: C, 51.59; H, 4.63; Br, 27.55.

Identification of Oleic Acid.—The *cis*-9-octadecenoic (oleic) acid was converted to 9,10-dihydroxystearic acid, m. p. 95° (lit.[7] m. p., 95°), with peracetic acid. This dihydroxystearic acid was oxidized with lead tetraacetate and the aldehyde obtained therefrom was further oxidized to pelargonic acid, m. p. 11° (lit.[13] m. p., 12.3°). The acid was identified as the *p*-bromophenacyl ester, m. p. 65.5° (lit.[14] m. p. 68.5°). *Anal.* Calcd. for $C_{17}H_{23}O_3Br$: C, 57.47; H, 6.53; Br, 22.50. Found: C, 57.21; H, 6.15; Br, 22.96. The aldehydoacid fraction was oxidized to azelaic acid and purified as above. The acid, m. p. 105°, neut. equiv. 93.7, was converted to the *p*-bromophenacyl ester, m. p. 129°. *Anal.* Calcd. for $C_{25}H_{26}O_6Br_2$: C, 51.56; H, 4.50; Br, 27.45. Found: C, 51.27; H, 4.92; Br, 27.69.

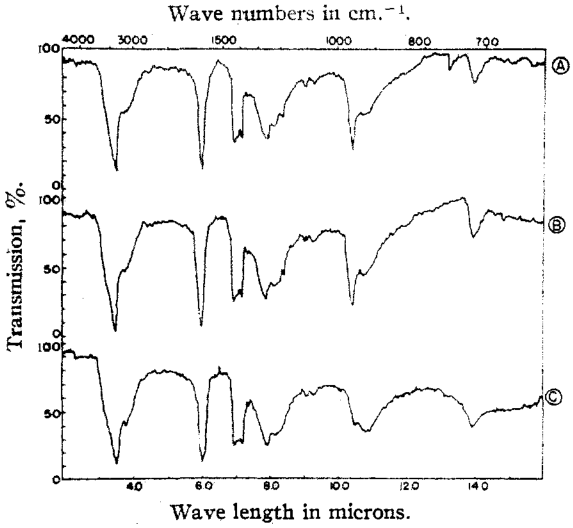

Fig. 1.—Infrared absorption curves: (A) *trans*-8-octadecenoic acid; (B) elaidic acid; (C) oleic acid.

Infrared Spectra.—Infrared absorption curves which present additional evidence for *cis* and *trans* configuration about a double bond were obtained for the three octadecenoic acids using a Baird recording infrared spectrophotometer.[17] The oleic acid was measured as a thin film between sodium chloride plates; *trans*-8 and *trans*-9-octadecenoic acids were run as 10% solutions in carbon tetrachloride using 0.01-cm. cells. The curves are given in Fig. 1.

Discussion

The location of the double bond in the isolated acids was proven by a partial oxidation to a dihydroxystearic acid followed by a mild cleavage of the chain between the two hydroxyl groups. By this procedure, *trans*-8-octadecenoic and elaidic acids were identified as two of the iso-oleic acids that were produced during this partial hydrogenation of triolein. The existence, however, of other iso-oleic acids in the reaction products is not excluded.

The conversion of *trans*-8-octadecenoic acid to the dihydroxystearic gave a new acid, 8,9-dihydroxystearic acid, m. p. 128°.

The evidence for a *trans* configuration of the two iso-acids is both chemical and physical. The *trans* monoenoic acids when converted to dihydroxystearic acids by the hydrogen peroxide–acetic acid–sulfuric acid method[7] give the higher melting isomers, melting points around 130°, whereas the *cis* acids give dihydroxystearic acid melting around 95°. The melting points of the known *trans* octadecenoic acids are all above 40° whereas the *cis* are 30° or below. Since the two isolated iso-acids gave higher melting dihydroxystearic acids and their own melting points are above 40°, they are *trans* in configuration.

Additional evidence for the *trans* configuration was obtained by infrared absorption analyses. The curves for the three acids are given in Fig. 1. It will be noted that the *trans* acids have a maximum absorption at 10.4 μ and the *cis* does not. This maximum absorption at 10.4 μ is indicative of a *trans* configuration.[18]

The formation of elaidic acid during the hydrogenation of triolein is in agreement with the results of Moore[3] and Hilditch and Vidyarthi[4] who found elaidic acid in the hydrogenation products of oleic acid esters. The presence of *trans*-8-octadecenoic acid was reported only by Hilditch and Vidyarthi.[4] An explanation why Moore[3] did not observe this acid may be that the permanganate oxidation may have oxidized the capric acid to pelargonic or caprylic acid.

On the basis of the rates of reaction one might expect 8-octadecenoic to be the predominating product. There is some experimental evidence[19] indicating that the ethylenic linkages located in different positions along the chain differ in their energy of activation and thus in their reactivity.

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(15) K. S. Markley, "Fatty Acids," Interscience Publishers, Inc., New York, N. Y., 1947, p. 434.

(16) T. L. Kelly and P. A. Kleff, THIS JOURNAL, **54**, 4444 (1932).

(17) The coöperation of Dr. Foil A. Miller of the Mellon Institute in obtaining the infrared absorption curves is gratefully acknowledged.

(18) P. C. Rao and B. F. Daubert, THIS JOURNAL, **70**, 1102 (1948).

(19) K. S. Markley, ref. 15, p. 363.

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 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.

PITTSBURGH, PA. RECEIVED MARCH 10, 1950

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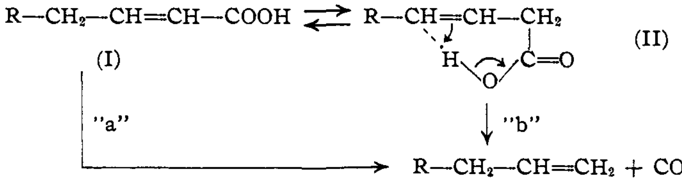
[20] G. V. Pigulevskii and P. A. Antamonox, *J. Gen. Chem. (USSR)*, **12**, 510 (1942).

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

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Thermal Decarboxylation of Unsaturated Acids

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



$R{-}CH_2{-}CH{=}CH{-}COOH \rightleftarrows R{-}CH{=}CH{-}CH_2{-}C({=}O){-}O{-}H$

$\rightarrow R{-}CH_2{-}CH{=}CH_2 + CO_2$

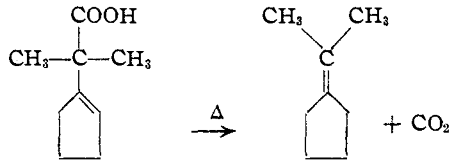
Carboxylic acids (and their derivatives) lose carbon dioxide under a variety of experimental conditions and undoubtedly by many different mechanisms. Several aspects of the decarboxylation reaction have been summarized[2] and the rôle of acid catalysis in the decomposition of cinnamic acid (and related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

An elegant study by Linstead and coworkers[4,5,6] has established the fact that through a simple prototropic shift α,β- and β,γ-unsaturated acids will frequently enter into mobile equilibrium. Linstead's work indicates that thermal decarboxylation of certain α,β-unsaturated acids may actually proceed *via* the β,γ-isomer as an intermediate.

It is an experimental fact that the olefins resulting from pyrolysis of simple α,β-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 β,γ isomer (II) which then decarboxylates through a cyclic transition complex as proposed for the thermal decomposition of β-keto acids.[7,8,9] It is the purpose of this paper to point out the fact that β,γ-unsaturated acids are thermally unstable and probably decarboxylate preferentially when in mobile thermodynamic equilibrium with the corresponding α,β-isomers.

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



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[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 α,β-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 β,γ-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).