

obtained with hydrogen may indicate that only secondary carbonium ions are active enough to react with hydrogen. Abstraction of a hydride ion from the hydrogen molecule by the secondary carbonium ion leads to the formation of *n*-butane as the primary C_4 product, which then slowly isomerizes to the equilibrium mixture.

Conclusion

A conventional carbonium-ion mechanism accounts for all the facts observed: the need for initiators and a high-dielectric medium, the increase in rate with acidity, the relative rates of conversion of the various isomers, the autocatalytic nature of the cracking reaction, and the change in rates with carbonium-ion concentration. Inhibitors provide a buffer that maintains the carbonium-ion concentration at a low but constant level, and thereby prevents run-away cracking.

The differences in ease of controlling side reactions when isomerizing paraffins other than hexanes are also in accord with this mechanism. A C_5 carbonium ion, when cracked to butane, forms 1.2 new carbonium ions; a C_6 ion gives 1.5 new ions; and a C_7 ion gives 1.75 new ions. Pentanes, hexanes, and heptanes require progressively higher concentration of inhibitors to react with the new carbonium ions as fast as they are formed and thereby prevent a net increase. In the case of heptanes and higher paraffins, it is difficult to add enough inhibitor to control the cracking reaction without stopping isomerization completely. Heptanes and higher paraffins are more susceptible to cracking also because direct breakdown of the heptyl cation to C_4 and C_3 fragments is possible; such breakdown need not be preceded by a dimerization step.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

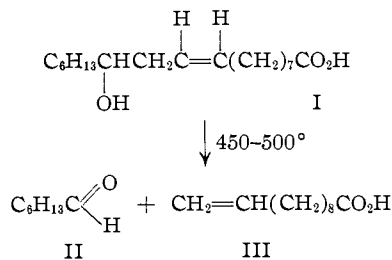
The Pyrolysis of β -Hydroxyolefins

BY RICHARD T. ARNOLD¹ AND GERALD SMOLINSKY²

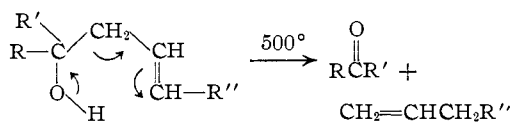
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In order to examine more fully the manner by which ricinoleic acid undergoes thermal decomposition into heptaldehyde and undecylenic acid, we have prepared a number of related β -hydroxyolefins and subjected these—for short periods of time in a flow system—to temperatures near 500°. The products formed in each case are readily explained in terms of a six-membered cyclic transition state.

Ricinoleic acid (I) and its derivatives form the major fatty acid components of castor oil. The pyrolysis of these substances^{3,4} furnishes the most convenient route to heptaldehyde (II) and undecylenic acid (III), and represents one of the most intriguing transformations of a naturally occurring compound.



Several years ago, one of us (R.T.A.)⁵ suggested that this decomposition probably occurs *via* a cyclic transition state as illustrated below for the general case.



- (1) Alfred P. Sloan Research Associate.
- (2) Postdoctorate Research Associate, 1958-1959.
- (3) C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc. (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 164.
- (4) A. A. Vernon and H. K. Ross, *THIS JOURNAL*, **58**, 2430 (1936).
- (5) This proposal was made during a talk before the Organic Division of the American Chemical Society in Boston, Mass., June, 1947.

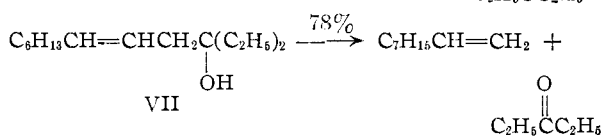
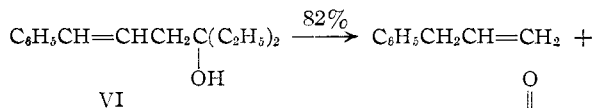
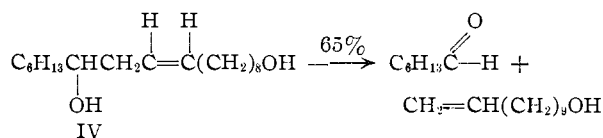
Although the concept of cyclic transition states has been commonly employed to explain the rearrangements of allylic systems,^{6,7} its use has certainly not been restricted to these examples.⁸⁻¹⁴ Of especial interest to us is the distinct possibility that the direct formation of unsaturated alcohols from olefins and aldehydes^{11,14} is essentially the reverse of the pyrolytic reaction described in this paper.

We have now been able to demonstrate that the thermal decomposition of ricinoleic acid in no way represents a unique situation but is perhaps only the best known example of what appears to be a very general reaction of β -hydroxyolefins.

Specifically, we have prepared the four unsaturated alcohols IV-VII and have shown that each of these substances undergoes a facile conversion at 500° to give quite respectable yields of products anticipated by the proposed mechanism.

An examination of molecular models indicates that the geometric configuration around the carbon-carbon double bond should have no appreciable effect on the course of the reaction. Our experi-

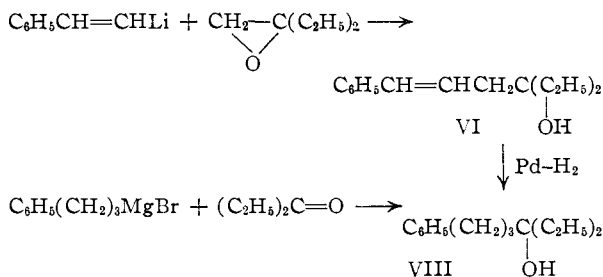
- (6) D. S. Tarbell, *Chem. Revs.*, **27**, 495 (1940).
- (7) A. C. Cope and L. Field, *THIS JOURNAL*, **71**, 1589 (1949), and earlier papers.
- (8) F. H. Westheimer and W. A. Jones, *ibid.*, **63**, 3283 (1941).
- (9) R. T. Arnold and M. J. Danzig, *ibid.*, **79**, 892 (1957).
- (10) R. T. Arnold and J. S. Showell, *ibid.*, **79**, 419 (1957).
- (11) R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2590 (1948).
- (12) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 343 (1956).
- (13) C. J. Albisetti, N. G. Fisher, M. J. Hogsed and R. M. Joyce, *THIS JOURNAL*, **78**, 2637 (1956).
- (14) M. Vilkas, G. Dupont and R. Delou, *Bull. soc. chim. France*, 799 (1955).



mental results support this view. Compound IV—which is derived from ricinoleic acid^{15,16} has a *cis* configuration. The method of synthesis and the infrared spectra of VI and VII leave little doubt that these compounds possess *trans* configurations.

The stereochemical demands imposed by the cyclic transition state suggest that the reaction under discussion is kinetically and not thermodynamically controlled. Evidence in support of this is found in the fact that methylenecyclohexane and allylbenzene are formed from the decomposition of V and VI, respectively, rather than the more stable isomeric hydrocarbons methylcyclohexene¹⁷ and propenylbenzene.

The unsaturated glycol IV was readily prepared by the reduction of methyl ricinoleate¹⁸ by means of lithium aluminum hydride. Compounds V, VI and VII were synthesized from the appropriate alkenyllithium derivatives and alkene oxides as illustrated below for VI.



Derivatives of ethylene oxide often rearrange to isomeric carbonyl compounds in the presence of organometallic compounds—and Grignard reagents in particular—prior to undergoing an addition reaction with these reagents.¹⁹

No evidence for such rearrangements was found in the present study. The nature of the products formed from the pyrolytic reactions testifies to the correctness of the structures assigned to compounds

(15) L. Crombie and A. G. Jacklin, *Chemistry & Industry*, 1197 (1954).

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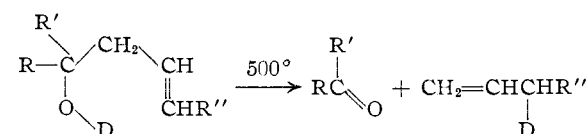
(17) R. B. Turner and R. H. Garner, *ibid.*, **79**, 253 (1957).

(18) We are indebted to Dr. Don S. Bolley, Baker Castor Oil Co., Bayonne, N. J., for a generous sample of this compound.

(19) N. G. Gaylord and L. D. Caul, *THIS JOURNAL*, **77**, 3132 (1955).

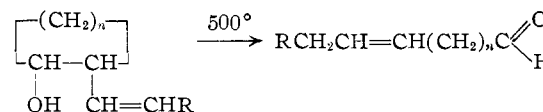
IV–VII. In addition, the hydrogenation of VI to VIII confirms the structure of this unsaturated alcohol.

The application of the cyclic transition state concept to the pyrolytic cleavage under study leads to two conclusions. In the first place, the β -hydroxyolefinic compound must possess at least one conformation in which the hydroxyl group can approach closely the π -electrons of the carbon-carbon double bond. If this condition is not satisfied, thermal dehydration of the unsaturated alcohol should take precedence over cleavage. Secondly, the hydrogen atom which undergoes migration should attach itself only to the carbon atom of the double bond furthest removed from the hydroxyl group, as shown below, using deuterium as a tracer element.



Experiments are currently under way to test each of these conclusions.

The ease with which β -hydroxyolefins undergo pyrolytic cleavage and the simplicity of the apparatus required, suggests that this reaction offers a new and general method for the lengthening of carbon chains as outlined below.



Initial experiments have already met with success, and a full report will be published when the scope of the reaction has been ascertained.

Experimental

9-Octadecene-1,12-diol (IV).—To lithium aluminum hydride (32 g.) in purified, dry tetrahydrofuran (3.5 l.) was added a solution of redistilled methyl ricinoleate (250 g.) in tetrahydrofuran (200 ml.). After the addition was complete, the reaction mixture was boiled overnight. The entire process was carried out in an atmosphere of nitrogen. Cautious addition of acetone destroyed the excess lithium aluminum hydride. Approximately one-half of the solvent was removed by distillation and sufficient saturated sodium potassium tartrate added to dissolve most of the inorganic residue, and the entire mixture was filtered. The filtrate was extracted with ether, and the ethereal solution was dried and distilled to give the desired glycol; yield 118 g. (52%), b.p. 178–185° (0.1 mm.). Redistillation gave the analytical sample, b.p. 158° (0.025 mm.), n_D^{25} 1.4722. The infrared spectrum (CCl_4) indicated the absence of ester, strong OH bands (3.05 μ) and weak C=C (6.1 μ).

Anal. Calcd. for $\text{C}_{18}\text{H}_{36}\text{O}_2$: C, 75.99; H, 12.76. Found: C, 75.90; H, 12.82.

1-(1'-Cyclohexenyl)-octanol-2 (V).—To a stirred suspension of freshly cut small pieces of lithium (3.26 g.) in dry ether (400 ml.) was added a solution of refractionated 1-chlorocyclohexene²⁰ (25 g.) in ether (100 ml.). The reaction was carried out in an atmosphere of nitrogen and allowed to proceed for 25 hours, although even after this period a small amount of lithium remained unreacted. To this mixture was added 1,2-epoxyoctane²¹ (15 g.) dissolved in dry ether (100 ml.). The reaction mixture was boiled for 24 hours in a nitrogen atmosphere, cooled and filtered to remove unreacted lithium. The filtrate was

(20) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2014 (1950).

(21) W. D. Emmons and A. S. Pagano, *THIS JOURNAL*, **77**, 89 (1955).

poured onto a slurry of ice and acetic acid (15 ml.). The ether phase was separated, washed with dilute sodium carbonate solution, dried and evaporated under reduced pressure. Distillation gave 18.4 g. of product, b.p. 105–110° (0.8 mm.). Careful fractionation of this material gave 10.8 g. (37%) 1-(1'-cyclohexenyl)-octanol-2, b.p. 132–133° (2.5 mm.), n_D^{25} 1.4753.

Anal. Calcd. for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 80.38; H, 12.58.

1,2-Epoxy-2-ethylbutane.—Although peroxytrifluoroacetic acid²¹ has been used with great success in this Laboratory for direct epoxidation, its reaction with 2-ethyl-1-butene gave a product containing about 30% of 2-ethylbutanal as proved by comparison of its infrared spectrum and 2,4-dinitrophenylhydrazine (m.p. 134–135°) with an authentic sample. The oxide was, however, prepared in 70% yield from the reaction of ethyl chloroacetate with ethylmagnesium bromide followed by treatment of the resulting chlorohydrin with solid potassium hydroxide using the procedure of Dalebroux and Wuyts.²²

3-Ethyl-6-phenylhexen-5-ol-3 (VI).—To a stirred, cold (0°) suspension of finely cut lithium (6.9 g.) in dry ether (400 ml.), under an atmosphere of nitrogen, was added a solution of β -bromostyrene (100 g.) in ether (100 ml.). The cold mixture was stirred for 8 hours, after which time most of the lithium had reacted, and the solution was deep red in color. To this cold solution was added 1,2-epoxy-2-ethylbutane (40 g.) dissolved in ether (50 ml.). The mixture was stirred at room temperature for one hour and then boiled for 13 hours. Filtration of the cooled reaction mixture removed unreacted lithium, and the filtrate was poured onto cracked ice and acetic acid (40 ml.). The ether phase was washed dried and evaporated. Distillation gave a crude product (20.5 g., b.p. 100–125° (0.5 mm.)) which was refractionated to give 15.4 g. (19%) of 3-ethyl-6-phenylhexen-5-ol-3, b.p. 115–117° (0.75 mm.), n_D^{25} 1.5430. The ultraviolet spectrum (in isoöctane) had three maxima: $\epsilon_{252m\mu}$ 20,430, $\epsilon_{285m\mu}$ 1,780 and $\epsilon_{294m\mu}$ 1,270.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.51; H, 9.99.

3-Ethyl-6-phenylhexanol-3 (VIII).—A solution of the above unsaturated alcohol (4.45 g.) in ethanol (50 ml., 95%) was hydrogenated at 50 p.s.i. using palladized carbon (1 g., 5%) as catalyst. After 24 hours, the catalyst was removed by filtration and the product isolated by distillation to give a quantitative yield; b.p. 119–120° (2 mm.). The infrared spectrum of this alcohol was identical with the one obtained from the reaction of pentanone-3 (17.2 g.) and the Grignard reagent from 1-bromo-3-phenylpropane (38 g.).

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.25; H, 10.82.

3-Ethyl-dodecen-5-ol-3 (VII) was prepared by the general method described above using the lithium derivative from 1-bromoöctene (48 g.) and 1,2-epoxy-2-ethylbutane (25 g.) in ether (250 ml.). The desired unsaturated alcohol was finally obtained by careful fractionation; yield 24.5 g. (46%), b.p. 114–115° (2 mm.), n_D^{25} 1.4584.

Anal. Calcd. for $C_{14}H_{26}O$: C, 79.18; H, 13.29. Found: C, 78.79; H, 13.03.

Pyrolysis.—All pyrolyses were carried out in the same manner. The furnace consisted of a glass helices-packed tube having an internal diameter of 20 mm. and heated for approximately 1' of its length at 500°. At the beginning of each run, the freshly cleaned pyrolysis tube was heated and

swept with nitrogen. The nitrogen stream was continued during the entire reaction. The compound to be pyrolyzed was added dropwise at a rate of approximately 30 g./hr.

Pyrolysis of 3-Ethyl-dodecen-5-ol-3 (VII).—The unsaturated alcohol (13.2 g.) was added dropwise with a slow stream of nitrogen over a period of 30 minutes to a glass helices-packed pyrolysis tube held at 500°. The total condensate was distilled to give the fractions: 1, b.p. 100–105° 4.17 g.; 2, b.p. 140–147° 6.06 g.; 3, residue 1.80 g.; total, 12.03 g. (91%).

Fraction 1 was identified as pentanone-3, yield 78%. Its infrared spectrum and 2,4-dinitrophenylhydrazine (m.p. 156°) were identical with those from an authentic sample. Fraction 2 was refractionated to give pure nonene-1 (5 g.), b.p. 144–146°, n_D^{15} 1.4149. Its infrared spectrum in CCl_4 showed a $C=CH_2$ band (6.12, 10.97 μ) of the proper intensity. Vapor phase chromatography²³ under conditions (retention time 2.8 minutes at 127°) which separated nonene-1 from *cis*- and *trans*-nonene-2 showed the nonene-1 to be free of these isomers. The high boiling residue from the fractionation consisted mainly of an unsaturated hydrocarbon (found: C, 84.53; H, 13.27) formed by dehydration of the starting material.

Pyrolysis of 9-Octadecen-1,12-diol (IV).—This unsaturated glycol (40.5 g.) was dropped (at 30 g./hr.) through a heated (500°) Pyrex tube packed with glass helices and swept with nitrogen. The condensate was directly fractionated to give heptaldehyde (9.8 g., b.p. 153–155°) identified by comparison of its infrared spectrum and 2,4-dinitrophenylhydrazine (m.p. 108°) with those from an authentic sample. There was also obtained Δ^{10} -undecenol-1 (14.5 g.), n_D^{25} 1.4504, b.p. 124–130° (23 mm.), m.p. –5°; reported n_D^{19} 1.4505,²⁴ m.p. –7°.²⁵

Pyrolysis of 1-(1'-Cyclohexyl)-2-octanol (V).—The unsaturated alcohol (12.5 g.) was pyrolyzed at 500° in the manner described above. The total condensate was fractionated to give heptaldehyde (4.98 g.) and methylenecyclohexane (4.46 g.), b.p. 104–106°. Vapor phase chromatography (retention time 3.8 minutes at 80°) showed this hydrocarbon to be homogeneous and free of 1-methylcyclohexene from which it could be readily separated. The infrared spectrum of the methylenecyclohexane was identical with that of an authentic sample.

Pyrolysis of 3-Ethyl-6-phenylhexen-5-ol-3 (VI).—Pyrolysis of this compound (14 g.) was carried out at 500° in the usual way. In addition to pentanone-3 (4.83 g., b.p. 101–103°), which was identified as described above, there was obtained an olefin (6.27 g.) identified as allylbenzene by its boiling point (154–156°) and by comparison of its infrared spectrum with that of an authentic sample. A careful examination of the ultraviolet spectrum of this olefinic product indicated the presence of not more than 12% of propenylbenzene formed, we believe, by subsequent isomerization of allylbenzene. In a separate experiment, pure allylbenzene was passed through the experimental pyrolysis tube at 500° at a flow rate of 30 g./hr. and shown to rearrange to propenylbenzene to the extent of 2%. These experimental conditions, however, are not identical with those present in the pyrolysis tube during the actual decomposition of the β -hydroxyolefins.

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(23) A Perkin-Elmer vapor phase fractometer (model 154) equipped with column C—having a length of two meters and a polysilicone liquid phase—was used throughout this study.

(24) P. Chuit, F. Boelsing, J. Hausser and G. Malet, *Helv. Chim. Acta*, **9**, 1074 (1926).

(25) A. Grün and T. Wirth, *Ber.*, **55**, 2206 (1922).

(22) R. Dalebroux and H. Wuyts, *Bull. soc. chim. Belg.*, **20**, 156 (1906).