m.p. 109–110° (lit.[12] m.p. 110°), which gave no depression in a mixed melting point with the 2,4-dinitrophenylhydrazone of authentic methyl acetoacetate.

Methyl β-hydroxybutyrate. β-Butyrolactone was prepared according to Johansson's[9] method of heating a well stirred aqueous solution of sodium β-bromobutyrate at 40° for 6 hr. with chloroform, replacing the chloroform several times during the heating period. The solution was maintained basic to bromthymol blue by addition of 10% sodium hydroxide as needed. The combined chloroform solutions were dried, the solvent evaporated, and the β-butyrolactone (55%) distilled under vacuum, b.p. 58–59°/15 mm. (lit.[9] b.p. 54.4–55/10 mm.). A carbonyl band at 1818 cm.$^{-1}$ confirmed the presence of the lactone structure[8] and hydrolysis[13] with methanolic sodium hydroxide at 0° followed by neutralization by dilute hydrochloric acid gave methyl β-hydroxybutyrate (54%), b.p. 56–58°/7 mm. (lit.[7] b.p. 67–68.5°/13 mm.).

The amide, prepared as above, had a m.p. of 84–85° (lit.[9] m.p. 84–87° and 83–84°[10]).

1-Methoxy-2-propanol and 2-methoxy-1-propanol. Propylene oxide (1 mole, 58 g.) and 250 ml. of methanol were heated to 130° in a sealed system[14] under a nitrogen atmosphere and held at this temperature for 2.5 hr. The reaction product was then removed and stripped of excess methanol and unchanged propylene oxide. Fractionation of the residue on an 18-in. Widmer column gave 24.6 g. of 1-methoxy-2-propanol, b.p. 53–55°/50 mm., 116–119°/1 atm. (lit.[15] b.p. 118–119°/1 atm.) and 9.8 g. of 2-methoxy-1-propanol, b.p. 58–59°/50 mm., 127–129°/1 atm. (lit.[15] b.p. 130°/1 atm.). The 2,4-dinitrobenzoate[11] of 1-methoxy-2-propanol melted at 73–76° (lit.[15] m.p. 83.5–85°). The same derivative prepared from authentic 1-methoxy-2-propanol (Dowanol PM) had a melting point of 74–77° and did not depress the melting point of the original material. Analysis by gas chromatography did not reveal any impurities in the authentic 1-methoxy-2-propanol and its infrared spectrum was the same as that of the compound prepared above.

2-Methoxy-1-propanol gave a 2,4-dinitrobenzoate which had m.p. 93–95° (lit.[15] m.p. 95.5–97°).

Acknowledgment. The authors would like to thank the Diamond Alkali Company for their support of this work.

IONICS, INCORPORATED
152 SIXTH STREET
CAMBRIDGE 42, MASS.

---

[11] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, 1948.

[12] N. M. Chopra, W. Cocker, B. E. Cross, J. T. Edwards, P. H. Hayes, and H. P. Hutchison, *J. Chem. Soc.*, 588 (1955).

[13] T. L. Gresham, J. E. Jansen, F. W. Shaver, J. T. Gregory, and W. L. Beears, *J. Am. Chem. Soc.*, **70**, 1004 (1948).

[14] H. C. Chitwood and B. T. Freure, *J. Am. Chem. Soc.*, **68**, 680 (1946).

[15] W. Reeve and A. Sadle, *J. Am. Chem. Soc.*, **72**, 1251 (1950).

Catalytic Hydrogenation of *cis*-6,7-Epoxyoctadecanoic Acid

SARA P. FORE AND W. G. BICKFORD[1]

Received July 27, 1960

The catalytic hydrogenation of 9,10-epoxyoctadecanoic acid and certain of its esters results in the selective formation of the 10-hydroxy derivative.[2–5] It was postulated that this reaction proceeds by a mechanism involving an oxonium ion intermediate and its specificity was attributed to the influence exerted at both the oxirane center and the catalyst surface by the electrophilic —COO— group.[4] More recently the hydrogenation of 9,10-epoxyoctadecyl acetate was investigated and it was found that 9- and 10-hydroxy isomers were formed in equimolar proportions.[6] The difference in results in these two instances was attributed to the relative positions of the oxirane centers with respect to the —COO— groups. It appeared of interest, therefore, to investigate the catalytic hydrogenation of a long chain epoxy acid in which the oxirane center was not situated at the 9,10-position. Accordingly, the catalytic hydrogenation of *cis*-6,7-epoxyoctadecanoic acid, obtained by epoxidation of petroselinic (*cis*-6-octadecanoic) acid, was investigated.

Attempts to hydrogenate alcoholic solutions of *cis*-6,7-epoxyoctadecanoic acid at room temperature and 20–30 pounds pressure employing either Raney nickel, Adams' catalyst, or 5% palladium on calcium carbonate were unsuccessful. However, under identical conditions it was found that hydrogenation could be readily effected through use of 10% palladium on carbon. It was also found that the theoretical amount of hydrogen was absorbed during quantitative hydrogenation[7] employing acetic acid as solvent and 10% palladium on carbon as catalyst. In general, the rate of hydrogenation of *cis*-6,7-epoxyoctadecanoic acid in ethanolic solution employing either 5 or 10% of 10% palladium on carbon catalyst was comparable to that observed for other long chain epoxides. However, in one experiment employing 10% of 10% palladium on carbon catalyst more than the theoretical quantity of hydrogen was absorbed and hydrogenation was complete in twelve minutes whereas several hours were generally required for complete hydrogenation.

The identity of the hydroxy acids resulting from the abnormally rapid hydrogenation and those from

---

[1] Deceased.

[2] G. V. Pigulevskiĭ and Z. Ya. Rubashko, *J. Gen. Chem. (U.S.S.R.)*, **9**, 829 (1939); *Chem. Abstr.*, **34**, 378 (1940).

[3] J. Ross, A. I. Gebhart, and J. F. Gerecht, *J. Am. Chem. Soc.*, **71**, 282 (1949).

[4] C. H. Mack and W. G. Bickford, *J. Org. Chem.*, **18**, 686 (1953).

[5] On the basis of recent data on the melting points of 9- and 10-oxooctadecanoic acids and their semicarbazones, F. J. Julietti, J. F. McGhie, B. L. Rao, and W. A. Ross, *Chem. & Ind.*, 874 (1960), conclude that a 2:3 mixture of 9- and 10-oxooctadecanoic acids is obtained on oxidation of the hydroxy acids resulting from hydrogenation of 9,10-epoxyoctadecanoic acid and thus this reaction is less selective than earlier workers believed.

[6] S. P. Fore and W. G. Bickford, *J. Org. Chem.*, **24**, 620 (1959).

[7] F. C. Pack, R. W. Planck, and F. G. Dollear, *J. Am. Oil Chemists' Soc.*, **29**, 227 (1952).

a slow hydrogenation was determined by the following series of reactions: the hydroxy acids were oxidized to the keto acids which were then converted to their oximes; the oximes were subjected to Beckmann rearrangement and the resultant amides were hydrolyzed under pressure with alkali; the mixed dicarboxylic acids recovered from the hydrolyzate were analyzed by application of elution chromatography employing a modification[8] of the method of Higuchi *et al.*[9] Both of the samples examined were found to contain approximately equimolar quantities of 6- and 7-hydroxyoctadecanoic acids. In addition, stearic acid was isolated from the crude oximes derived from the product of the rapid hydrogenation and the analysis of this sample and its derivatives indicated that up to 40% of stearic acid was formed during this hydrogenation.

The catalytic hydrogenation of *cis*-6,7-epoxyoctadecanoic acid differs from that of 9,10-epoxyoctadecanoic acid. Evidently the spatial relation between the oxirane center and the acyl oxygen of the 6,7-epoxyoctadecanoic acid does not permit the operation of the influence of the —COO— group observed in the case of 9,10-epoxyoctadecanoic acid.

EXPERIMENTAL

Epoxidation procedure. Petroselinic acid[10] (56.4 g., 0.20 mole, I. V., 89.4) was stirred and maintained at 15–20° during the dropwise addition, over a period of 1 hr., of 34.1 ml. of 40% peracetic acid (0.23 mole). The reaction mixture was stirred at *ca.* 25° for another 2 hr. and then was poured into 500 ml. of water. The crystalline epoxide was recovered by filtration, washed with 1000 ml. of cold distilled water, and crystallized, first from four volumes of petroleum ether (b.p. 35–60°) and then twice from ten volumes of acetone at −25°. The *cis*-6,7-epoxyoctadecanoic acid thus obtained (40.8 g.) melted at 58.5–59.3°.

Anal. Calcd. for $C_{18}H_{34}O_3$: C, 72.43; H, 11.48; Oxirane O, 5.36. Found: C, 72.63; H, 11.55; Oxirane O, 5.32.

Hydrogenation procedure. All hydrogenations, with the exception of the analytical hydrogenation, were carried out in a shaking type hydrogenation apparatus at an initial hydrogen pressure of 28–30 pounds and employing five volumes of ethanol as solvent and 5 or 10% of catalyst.

A typical hydrogenation experiment, carried out as described above employing 14.9 g. of epoxy acid and 0.76 g. of 10% palladium on carbon catalyst, required about 40 hr. to complete and absorbed approximately the theoretical quantity of hydrogen. The recovered product (14.4 g.) melted at 68–70°.

Anal. Calcd. for $C_{18}H_{36}O_3$: C, 71.95; H, 12.08; OH, 5.66; neut. equiv., 300.5. Found: C, 72.30; H, 12.37; OH, 4.72; neut. equiv., 305.7.

One hydrogenation employing 10% of 10% palladium on carbon absorbed 1.3 times the theoretical quantity of hydrogen and was abnormally rapid, requiring only 12 min. for the hydrogenation of 29.8 g. of epoxy acid, but when duplication of these results was attempted with 10.0 g. of the same epoxide only the theoretical quantity of hydrogen was absorbed and the time required for the hydrogenation was 4 hr. The reaction product (27.6 g.) recovered from the fast hydrogenation melted at 65–66°.

Anal. Found: C, 73.79; H, 12.35; OH, 3.15; neut. equiv., 303.1.

Identification of hydroxy acids. The methods used for preparation of keto acids and their oximes, for the Beckmann rearrangement and for hydrolysis of amides have been described in detail elsewhere.[11] Pertinent details regarding the application of these reactions to the hydroxy acids from one of the normal (slow) hydrogenations of *cis*-6,7-epoxyoctadecanoic acid are given below.

cis-6(7)-Hydroxyoctadecanoic acid (10.6 g.) was converted to 6(7)-oxooctadecanoic acid (9.8 g.) by oxidation with chromium trioxide.

Anal. Calcd. for $C_{18}H_{34}O_3$: Carbonyl O, 5.36. Found: Carbonyl O, 5.15.

The keto acid (8.96 g.) on treatment with hydroxylamine hydrochloride yielded the oxime (9.11 g.).

Anal. Calcd. for $C_{18}H_{35}NO_3$: N, 4.47. Found: N, 4.06.

Beckmann rearrangement of 8.85 g. of oximes yielded 9.40 g. of amides, 4.4 g. of which were subjected to alkaline hydrolysis.

The hydrolyzate was transferred to a separatory funnel with 100 ml. of water, acidified with 23.0 ml. of concd. hydrochloric acid, and washed three times with 50-ml. portions of petroleum ether (b.p. 35–60°). The combined petroleum ether solutions were concentrated to 50 ml. and washed with 50 and then 25 ml. of water. These water washings, along with emulsified material which formed during the second washing, were added to the main aqueous phase and this was extracted six times with diethyl ether. The ether solution was dried over sodium sulfate and filtered and the ether was removed by heating on a steam cone under a stream of nitrogen gas. When extraction of the dicarboxylic acids from the residue (2.26 g.) with boiling water was attempted, the water insoluble portion became dispersed throughout the water and no separation could be made. A 0.73-g. sample of the oily, brown solid (1.62 g.) remaining after removal of the water was dissolved in 5.0 ml. of *tert*-amyl alcohol and diluted to 50.0 ml. with chloroform. A 3.0-ml. aliquot of this solution was analyzed chromatographically by the modification of the method of Higuchi *et al.*[9] described by Chahine *et al.*[8] The sample contained only two dibasic acids, pimelic and adipic acids, and these were present in equimolar quantities (0.061 mmole of each acid in the 3.0-ml. aliquot).

When this same series of reactions was applied to the hydroxy acids from the abnormal (fast) hydrogenation, pimelic and adipic acids were isolated in a molar ratio of 1 to 1.2.

Isolation of stearic acid. A sample of the oximes (1.47 g.) derived from the product of the abnormal (fast) hydrogenation which was dissolved by warming in 100 ml. of 70% ethanol deposited 0.43 g. of crystals (m.p. 69.3–70.5°) on standing for 16 hr. at 25°. Recrystallization of 0.33 g. of this material from 3 ml. of methanol afforded 0.26 g. of stearic acid (m.p. 70.2–71.4°). No depression of melting point was observed on admixture of either of these samples with authentic stearic acid.

Acknowledgment. The authors express their appreciation to L. E. Brown, Vidabelle O. Cirino, and Alva F. Cucullu for certain of the analyses.

SOUTHERN REGIONAL RESEARCH LABORATORY[12]
NEW ORLEANS, LA.

---

[8] M. H. Chahine, E. R. Cousins, and R. O. Feuge, *J. Am. Oil Chemists' Soc.*, **35**, 396 (1958).

[9] T. Higuchi, N. C. Hill, and G. B. Corcoran, *Anal. Chem.*, **24**, 491 (1952).

[10] S. P. Fore, R. L. Holmes, and W. G. Bickford, *J. Am. Oil Chemists' Soc.*, **37**, 490 (1960).

[11] S. P. Fore and W. G. Bickford, *J. Org. Chem.*, **24**, 920 (1959).

[12] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.