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The Selective Hydrogenation of Unsaturated Esters to Unsaturated Alcohols

BY JOHN SAUER AND HOMER ADKINS

The hydrogenation of the double bond in such a compound as ethyl oleate is readily accomplished at room temperatures and atmospheric pressures of hydrogen over nickel, platinum or palladium catalysts. In order to bring about satisfactorily the hydrogenation of a carbalkoxy to a carbinol group temperatures in excess of 200° and pressures of the order of 100 atmospheres are required. In other words the alkene linkage reacts with hydrogen under conditions which are as mild as are used in any catalytic hydrogenation, while the carbalkoxy group requires drastic conditions. However, it seemed worth while to attempt the selective hydrogenation of the carbalkoxy groups with certain of the metallic oxides which are relatively inactive in the catalysis of the hydrogenation of alkene linkages.[1]

There are recorded in Table I the results obtained with six such catalysts containing zinc or copper combined with chromium, vanadium or molybdenum. Ethyl or butyl oleates were used in testing the catalysts. The butyl ester is very much to be preferred for this purpose since the ethyl esters boil at so nearly the same temperature as the alcohols that it is difficult to separate the ester from the alcohols.

It may be seen from the data in the table that copper–molybdenum oxide induced the hydrogenation of the double bond with the formation of ethyl stearate, while copper–chromium oxide caused the addition of three moles of hydrogen with the formation of octadecanol. Zinc–chromium oxide was, however, relatively inactive toward the alkene linkage and reasonably active toward the carbalkoxy group so that the unsaturated alcohol $C_{17}H_{33}CH_2OH$ was obtained in yields of over 60%. An unsaturated alcohol $C_{21}H_{41}CH_2OH$ was obtained in similar yield from butyl erucate. Zinc–vanadium oxide and zinc–molybdenum oxide were similar but inferior to zinc–chromium oxide for the production of the unsaturated alcohol.

Thus it is seen to be feasible to prepare unsaturated alcohols by the hydrogenation of certain unsaturated esters. However, the process is not very satisfactory from a preparational standpoint. A very high ratio of catalyst to ester must be used. It is probable that one part of catalyst should be used for two parts of ester. The temperature required for adequate reaction is quite high (300°) and even so seven to eleven hours were required for relatively complete reactions. These factors have made it impossible to obtain yields higher than 68% of the unsaturated alcohol and in the case of the ester of undecen-10-oic acid, the yield was only 37%. The unsaturated alcohol produced by this process is always accompanied by small amounts of saturated alcohol which it appears cannot be readily separated from the unsaturated alcohol by fractionation. The process apparently is not applicable to esters

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[1] Lazier and Vaughen, THIS JOURNAL, **53**, 3719 (1931); **54**, 3080 (1932).

TABLE I

HYDROGENATION OF UNSATURATED ESTERS

Ester	G.	G.	Catalyst	Temp., °C.	Time hrs.	Moles H_2 per mole ester	% yield of products	
Bu oleate	86	50	Zn–Cr–O	300	11	1.86	65	octadecenol[a]
Bu oleate	129	71	Zn–Cr–O	283	11	..	63	octadecenol
Bu oleate	65	32	Zn–Cr–O	282	8	1.87	46	octadecenol
							34	octadecenyl oleate
Bu erucate	50	25	Zn–Cr–O	295	7	1.82	68	ducosenol[b]
Bu undecen-10-oate	43	21	Zn–Cr–O	293	11	1.63	37	undecenol[c]
Bu oleate	65	6.5	Cu–Cr–O	250	..	2.97	86	octadecanol
Et oleate	65	20	Zn–V–O	300	5	1.15	55	octadecenyl oleate
Et oleate	65	20	Zn–Mo–O	280	4	..	67	octadecenol and Et oleate
Et oleate	65	7.5	Cu–Mo–O	250	4	1.32	70	Et stearate
Et oleate	65	7.5	Cu–V–O	275	5	2.20	8–10	octadecanol-1
							63	octadecyl stearate
Et oleate	65	20	Zn–Cr–O	300	5	1.30	50–60	octadecenol[d]

[a] B. p. 158° (2 mm.), n^{20}D 1.4605, after refractionation 1.4579. [b] B. p. 196° (3 mm.), m. p. 34–35°. [c] B. p. 133° (16 mm.), n^{19}D 1.4500, after refractionation 1.4473, phenylurethan m. p. 54–55°. [d] Contained small amount of Et oleate.

TABLE II

ANALYSIS OF ESTERS

Name of compd.	Formula	Mol. wt. Calcd.	Mol. wt. Found	B. p., °C.	Mm.	n^{25}D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Butyl erucate	$C_{21}H_{41}CO_2C_4H_9$	394	395	211–212	1	1.4538	79.13	79.06	12.73	12.95
Octadecyl stearate	$C_{17}H_{35}CO_2C_{18}H_{37}$	536	539	M. p. 62°		....	80.52	80.55	13.51	13.71
n-Butyl undecen-10-oate	$C_{10}H_{19}CO_2C_4H_9$	240	240	116	2	1.4391	74.93	74.97	11.74	12.15
Octadecenyl oleate	$C_{17}H_{33}CO_2C_{18}H_{35}$[a]	532	539	272	1	1.4618	...	...	...	...

[a] Meyer and Lühdemann, *Helv. Chim. Acta*, **18**, 307 (1935).

such as butyl penten-4-oate and ethyl cinnamate which have their double bond near the carbalkoxy group.

The catalysts were prepared by the same general process[2] previously used. The details for preparing zinc-chromium oxide are as follows: 250 g. of ammonium dichromate (1.0 *M*) was dissolved in 600 cc. of water and concd. ammonium hydroxide added until the liquid changed from orange to yellow (400 cc. of concd. ammonium hydroxide). To this solution was added 379 g. (2.0 *M*) of zinc nitrate dissolved in 800 cc. of water. The yellow precipitate (333 g.) was filtered, washed and dried overnight in an oven at 85°. The dried precipitate was decomposed in four portions, washed in 5% acetic acid for several minutes, filtered and dried overnight in an oven at 85°. The final yield of a brown colored catalyst was 220 g.

The oleates were prepared by the alcoholysis of olive oil.[3] Butyl erucate was similarly prepared from rapeseed oil. Butyl undecen-10-oate was prepared from the acid (b. p. 141–143° at 13 mm.)[4] according to a standard method.[5] The hydrogenations were carried out at 200 atmospheres by the standard method.[6] The products were separated by fractionation. The alcohols were shown to be ester free and the yields are based upon iodine numbers for the unsaturated alcohols. The samples of octadecenol,[7] ducosenol,[7] and undecenol[8] referred to in Table I contained 13, 3 and 9%, respectively, of the corresponding saturated alcohols. The octadecenol and ducosenol were also characterized by hydrogenation to octadecanol and ducosanol, m. p. 57–58° and 69°, respectively.

Summary

It has been shown that butyl oleate or butyl erucate may be hydrogenated over zinc–chromium

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(2) Lazier, U. S. Patent 1,746,783 (1930); Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1138 (1932).

(3) E. E. Reid, "Org. Syntheses," John Wiley and Sons, New York City, Vol. XV, 1935, p. 51.

(4) Kraft, *Ber.*, **10**, 2034 (1877).

(5) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York City, 1932, p. 256.

(6) Folkers and Adkins, THIS JOURNAL, **54**, 1145 (1932).

(7) Willstätter and Mayer, *Ber.*, **41**, 1478 (1908); Willstätter, Mayer and Hüni, *Ann.*, **378**, 101 (1911).

(8) Bouveault and Blanc, *Bull. soc. chim.*, [3] **31**, 1210 (1904); Chuit, Boelsing, Hausser and Malet, *Helv. Chim. Acta*, **9**, 1074 (1926).

oxide at 300° to give the corresponding unsaturated alcohol octadecenol or ducosenol in yields of above 60%.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY]

Studies on the Chemistry of the Fatty Acids. I. The Purification of Linoleic Acid by Crystallization Methods[1]

BY J. B. BROWN AND GEORGE G. STONER

On account of the recently discovered nutritional significance of linoleic acid, $C_{18}H_{32}O_2$, interest in its chemistry has increased greatly during the past few years. The acid occurs naturally in large amounts in the semi-drying oils, especially such oils as cottonseed, corn, soy bean and wheat germ. Despite several investigations on the subject there is still some question whether the acid occurs in these oils as a single geometric isomer or whether it occurs along with one or more of the other three possible forms. (We are considering here only the 9-10, 12-13, octadecadienoic acids although the possibility of other dienoic acids is not precluded.) One reason for this uncertainty is the fact that so far only one method has been available for preparing the pure acid, namely, that of Rollett.[2] In this method the mixed fatty acids of an oil are brominated in cold ether, the petroleum ether-insoluble bromides are isolated and purified and the linoleic acid is regenerated by heating with zinc dust. The product is satisfactory and is designated as α-linoleic acid.

Preparation of the acid by Rollett's method is unsatisfactory from the standpoint of yield, since in the bromination process considerable amounts of material are converted into petroleum ether-soluble isomeric bromides which are lost, and from the standpoint of chemical identity, since there is the question of alteration of the acid during bromination and debromination.

The object of the present work was to prepare linoleic acid by direct crystallization methods which did not involve bromination. As raw materials we have employed the fatty acids of refined cottonseed and corn oils containing approximately 50% of linoleic acid, the other acids present being principally palmitic and oleic.

Crystallization of cottonseed fatty acids from methyl alcohol, 95% ethyl alcohol, petroleum ether and acetone at −20° gave separations of saturated and unsaturated acids with an efficiency approaching that of the widely used lead soap–ether method. Fractional crystallization of cottonseed and corn oil fatty acids from acetone gave linoleic acid preparations 80–93% pure. The chief obstacle to the isolation of purer specimens is the fact that in attempting to obtain the more soluble constituent in every case, the product was always contaminated with oleic acid in proportion to the ratio of the solubility of linoleic acid to oleic acid under the experimental conditions. Crystallization of fatty acid mixtures at low temperatures constitutes a valuable method for the separation of these acids.

A large number of soap separations were tried. Of these, crystallization of the lithium soaps of cottonseed oil fatty acids from *n*-butanol at −20° gave 81% linoleic acid in the filtrate.

Experimental

Materials.—The sources of the fatty acids used in this work were commercial refined cottonseed and corn oils. The following analytical data were obtained on these oils.

	Cottonseed	Corn
	Original oil	
Saponification no.	194.5	194.0
Iodine no.[a]	112.0	129.9
	Fatty acids	
Mean mol. wt.	276	282.9
Iodine no.	119	133.8

[a] All iodine numbers determined by the Wijs method.

Typical analyses of these oils have shown the following fatty acid composition.

	Cottonseed[a]	Corn[b]
Linoleic	45–50	39.1
Oleic	25–30	43.4
Myristic	Small amount	. .
Palmitic	19.8	7.3

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[1] Presented at the September, 1936, meeting of the American Chemical Society.

[2] A. Rollett, *Z. physiol. Chem.*, **62**, 410 (1909).