1% sodium chloride solution it was noted that the salt removed about five times more nicotine. The successive portions of water and salt solution removed decreasing amounts of nicotine. Five grams of fully saturated bentonite lost about 20% of its nicotine when in contact with 200 cc. of salt solution. The experiments further substantiate the reverse effect of inorganic salt cations. It is quite probable that an equilibrium may not have been reached in these experiments, and a further study will be made of the reverse effect of salt solutions.

Summary

1. The reaction between bentonite and salts of organic bases is principally one of base exchange.
2. Bentonite enters into base exchange with a definite chemical equivalent of organic bases where saturation can be reached. In the one sample of bentonite used one gram combined with 6.2 to 6.4 cc. of 0.1 *N* organic base.
3. When saturation is approached with most bases flocculation is produced. Flocculation indicates that a reaction has taken place with partial or complete saturation of the silicate.
4. Saturation is promoted by the insolubility of the silicate complex and by removal of the inorganic salts by washing.

WASHINGTON, D. C. RECEIVED MARCH 9, 1934

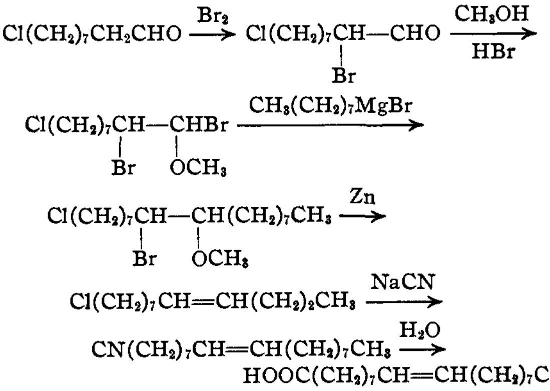
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Synthesis of Unsaturated Fatty Acids. Synthesis of Oleic and Elaidic Acids

BY C. R. NOLLER AND R. A. BANNEROT

In view of the difficulty of isolating pure unsaturated fatty acids from natural sources and the fact that the methods of synthesis commonly used lead to mixtures of structural isomers, a general method of synthesis yielding products free of structural isomers should be of value. It appears from an examination of the literature that even oleic acid has not been synthesized in such a way as to definitely place the position of the double bond. Thus it has merely been obtained as one of the products of the dehydration of 10-hydroxystearic acid or of the action of alcoholic potassium hydroxide on 10-iodostearic acid.[1] Both 10-hydroxystearic and 10-iodostearic acids have been obtained from 10-ketostearic acid, which has been synthesized.[2] The preparation of oleic and elaidic acids from stearolic acid[2,3] can hardly be termed a synthesis since stearolic acid has not been synthesized and was presumably obtained from natural oleic acid.

By making use of the Boord olefin synthesis[4] it has been possible to synthesize a mixture of oleic and elaidic acids in satisfactory yields. The reactions used were as follows



$$\mathrm{Cl(CH_2)_7CH_2CHO} \xrightarrow{\mathrm{Br_2}} \mathrm{Cl(CH_2)_7}\underset{\substack{|\\ \mathrm{Br}}}{\mathrm{CH}}\mathrm{{-}CHO} \xrightarrow[\mathrm{HBr}]{\mathrm{CH_3OH}}$$

$$\mathrm{Cl(CH_2)_7}\underset{\substack{|\\ \mathrm{Br}}}{\mathrm{CH}}\mathrm{{-}}\underset{\substack{|\\ \mathrm{OCH_3}}}{\mathrm{CHBr}} \xrightarrow{\mathrm{CH_3(CH_2)_7MgBr}}$$

$$\mathrm{Cl(CH_2)_7}\underset{\substack{|\\ \mathrm{Br}}}{\mathrm{CH}}\mathrm{{-}}\underset{\substack{|\\ \mathrm{OCH_3}}}{\mathrm{CH}}\mathrm{(CH_2)_7CH_3} \xrightarrow{\mathrm{Zn}}$$

$$\mathrm{Cl(CH_2)_7CH{=}CH(CH_2)_2CH_3} \xrightarrow{\mathrm{NaCN}}$$

$$\mathrm{CN(CH_2)_7CH{=}CH(CH_2)_7CH_3} \xrightarrow{\mathrm{H_2O}}$$

$$\mathrm{HOOC(CH_2)_7CH{=}CH(CH_2)_7CH_3}$$

Strictly speaking this is not a complete synthesis since the starting material was obtained by the series of reactions

$$\text{Butyl oleate} \xrightarrow[\text{alcohol}]{\mathrm{Na}} \text{oleyl alcohol} \xrightarrow{\mathrm{SOCl_2}}$$

$$\text{9,10-octadecenyl chloride} \xrightarrow{\mathrm{O_3}} \omega\text{-chlorononylaldehyde}$$

However, since azelaic acid has been obtained by the ozonation of oleic acid[5] and has been synthesized by several methods,[6] there seemed no urgent need for the synthesis of ω-chlorononylaldehyde.

It is interesting to note that the synthetic mixture of acids contained approximately 63% of elaidic acid which is in fair agreement with the

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(1) M., C., and A. Saizew, *J. prakt. Chem.*, [2] **35**, 385 (1887); Saizew and Lebedew, *ibid.*, **50**, 61 (1894); Arnaud and Posternak, *Compt. rend.*, **150**, 1525 (1910); Veseley and Majtl, *Bull. soc. chim.*, [4] **39**, 230 (1926).

(2) Robinson and Robinson, *J. Chem. Soc.*, **127**, 175 (1925).

(3) González, *Anales soc. españ. fís. quím.*, **24**, 156 (1926); *Chem. Centr.* II, 183 (1926); Paal and Schiedewitz, *Ber.*, **63**, 770 (1930).

(4) Shoemaker and Boord, THIS JOURNAL, **53**, 1505 (1931).

(5) Harries and Thieme, *Ann.*, **343**, 355 (1905).

(6) Haworth and Perkin, *Ber.*, **26**, 2249 (1893); v. Pechmann and Sidgwick, *ibid.*, **37**, 3821 (1904); Reformatsky, Grischkewitsch and Semenzow, *ibid.*, **44**, 1886 (1911); Dionneau, *Ann. chim.*, [9] **3**, 249 (1915).

results of Griffiths and Hilditch,[7] who found from inversion experiments that the equilibrium mixture contains 34% oleic and 66% of elaidic acid.

9,10-Octadecenyl Chloride.—In a one-liter three-necked flask equipped with a mechanical stirrer, dropping funnel and reflux condenser, were placed 134 g. of oleyl alcohol (prepared by the reduction of butyl oleate with sodium in butyl alcohol), 150 cc. of benzene and 0.25 cc. of pyridine.[8] The solution was cooled to 0° and 91 g. of thionyl chloride added over a period of five minutes with stirring and without further cooling. The temperature rose to about 30°. The solution was heated rapidly to boiling, the heating being discontinued if the evolution of sulfur dioxide became too rapid. Refluxing was continued for ten minutes after sulfur dioxide was no longer evolved at an appreciable rate. After cooling 250 cc. of a 10% sodium chloride solution was added with stirring and the whole transferred to a separatory funnel where the aqueous phase was removed. The aqueous layer was clarified by centrifuging and the oil obtained added to the upper layer. This was washed successively with 100 cc. of 10% sodium carbonate solution and 200 cc. of 10% sodium chloride solution, centrifuging when necessary. After removing the benzene, a single fractionation yielded 111 g. boiling at 165.5–168.5° at 3 mm. Redistillation of the high fractions gave an additional 7 g., bringing the total yield to 82% of the calculated amount.

The pure compound boils at 165° at 3 mm.; d_4^{25} 0.8704; n_D^{25} 1.4586; Cl, 12.36%; iodine number, 87.6. Calcd. for $C_{18}H_{35}Cl$: Cl, 12.38, iodine number, 88.5.

ω-Chlorononylaldehyde.—Ozonation of 9,10-octadecenyl chloride was carried out according to the procedure given by Adams and Noller[9] except that about twice the recommended amount of water was used during the decomposition of the ozonide. The yield from a 0.75 mole run was 88 g., b. p. 97–102 at 3 mm., or 66% of the calculated amount. On redistillation the main portion distilled at 100° at 3 mm.; d_4^{25} 0.9718; n_D^{25} 1.4501; Cl, 19.98. Calcd. for $C_9H_{17}OCl$: Cl, 20.10.

8,9-Dibromo-9-methoxynonyl Chloride.—A solution of 86 g. of ω-chlorononylaldehyde and 50 cc. of carbon tetrachloride was cooled to 0° and 85 g. of bromine added as fast as the solution decolorized, keeping the temperature below 5°. The reaction was quite slow, especially toward the end, so that the temperature was allowed to rise to 10°. The total time for the addition was five hours. To the mixture was next added 67 g. of absolute methyl alcohol over a period of thirty minutes, keeping the temperature at 10°. Finally dry hydrogen bromide was introduced under the surface at 10° for one hour, giving a nearly saturated solution.[10] The aqueous phase had so nearly the same density as the carbon tetrachloride layer that 5 cc. more methyl alcohol was added to cause a separation. The lower layer was perfectly colorless. After separation a little ice was added to the aqueous layer and 3 to 4 cc. more of slightly yellow oil obtained. The water insoluble layers were combined and the solvent distilled at room temperature for one hour at 22 mm. The flask was then evacuated at 4 mm. for four hours with vigorous mechanical shaking. The clear light amber product weighed 169 g. and was used in the following reaction without further purification.

8-Bromo-9-methoxyheptadecyl Chloride.—In spite of the careful evacuation early runs indicated that considerably more than an equivalent amount of Grignard reagent was necessary to react with the dibromo ether, probably because the hydrogen bromide and alcohol had not been completely removed. It was found that the reaction of Grignard reagent and dibromo ether proceeded rapidly to a definite end-point and the dibromo ether actually could be titrated with the Grignard reagent.

The dibromo ether was diluted with absolute ether to 250 cc. and placed in a graduated cylindrical dropping funnel attached to a three-necked flask equipped with a mechanical stirrer and thermometer. About 0.4 mole of standardized octylmagnesium bromide solution (approx. 0.002 mole per cc.) was introduced into the flask and cooled to 5–10°. About half of the dibromo ether solution was then slowly added and the mixture stirred for ten minutes. Gilman's test for Grignard reagent[11] was then applied, the required reagent added and after ten minutes a second test was made. After repeating this procedure a few times a reversible end-point was reached. From the data so obtained the required amount of Grignard reagent for the balance of the dibromo ether was calculated and the two reacted in the proper proportions. The mixture was finally allowed to warm up to room temperature and stirred for 1.5 hours after which it still showed a positive test for Grignard reagent. Even with carefully prepared dibromo ether, as much as 33% excess over the expected amount of Grignard reagent was required. The mixture was decomposed with ice and hydrochloric acid and the product after washing and evaporation of the ether was evacuated for two hours at 60° and 20 mm. It was pale amber in color and weighed 202 g.

8,9-Heptadecenyl Chloride.—The above product without further purification was dissolved in 400 cc. of dry butyl alcohol and refluxed for ten hours with 100 g. of 90–95% zinc dust. After removal of the zinc, the solution was washed with hydrochloric acid and water and distilled. After two fractionations there was obtained 30.5 g. boiling at 143–149° at 2 mm.

Anal. Calcd. for $C_{17}H_{33}Cl$: Cl, 13.01; iodine no., 93.03. Found: Cl, 12.36; iodine no., 87.9.

These analyses indicate that this product had 94.5% of the calculated amount of unsaturation and 95.0% of the required amount of halogen. Assuming 95% purity the yield of 8,9-heptadecenyl chloride based on the ω-chlorononylaldehyde is 22%.

8,9-Heptadecenyl Cyanide and 9,10-Octadecenoic Acids.—A mixture of 29 g. of heptadecenyl chloride, 13 g.

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[7] Griffiths and Hilditch, *J. Chem. Soc.*, 2315 (1932).

[8] Experiment showed that the use of a very small amount of pyridine gave much better results than when thionyl chloride alone or thionyl chloride and larger quantities of pyridine were used.

[9] Adams and Noller, This Journal, **48**, 1074 (1926).

[10] This is essentially the procedure of Späth and Göhring, *Monatsh.*, **41**, 319 (1920). If the modification of Schmitt and Boord, This Journal, **54**, 751 (1932), is used in which the methyl alcohol is added before bromination, no bromination takes place at all until all of the bromine is added and then the reaction occurs very rapidly. Bromination of the aldehyde alone takes place slowly but at a uniform rate.

[11] Gilman and co-workers, *ibid.*, **47**, 2002 (1925); **52**, 4949 (1930).

of powdered sodium cyanide and 225 cc. of 95% alcohol was refluxed for ninety hours. All of the chloride and most of the sodium cyanide were initially in solution. After refluxing, the solution was decanted and the insoluble salts washed with alcohol.

The combined alcoholic solutions were returned to the flask along with 8 g. of sodium hydroxide in 25 cc. of water and refluxed for ninety-six hours. The product was evaporated to dryness on the steam-bath, granulated, and dried at 105° to remove the alcohol. The dried soap was dissolved in hot water, acidified with hydrochloric acid and extracted with ether. The ether solution was washed with water and evaporated on the steam-bath. The residue was a light colored oil weighing 29.9 g.

The mixed acids were dissolved in 700 cc. of 95% alcohol and 9 g. of anhydrous lead acetate dissolved by heating. On standing overnight at 25°, 20.1 g. of precipitate was obtained which melted at 83–88°. By cooling to 0° a further crop of 1.0 g. melting at 80–83° was obtained. In the filtrate was dissolved an additional 4 g. of lead acetate. On cooling to 0°, 4.6 g. melting at 60–70° was obtained making a total yield of 25.7 g. of crude salt equivalent to 18.8 g. of elaidic acid or 63% of the mixed acids.

The filtrates containing the oleic acid were combined and concentrated to 190 cc. On cooling to 0°, 0.5 g. of gum precipitated which was probably largely lead oleate and was discarded. The filtrate was evaporated to dryness, taken up in ether, washed with dilute nitric acid and water and the ether evaporated. The residual oil, weighing 10.1 g., was dissolved in 275 cc. of 95% alcohol, 1 g. of lithium hydroxide dissolved by heating, and the solution filtered hot. Four crops of lithium oleate were taken, the first at 25° and the rest at 0° with progressive concentration of the solution. The combined weight was 6.1 g., the first crop melting at 225° and the last at 223°. The calculated amount of liquid acid was obtained from the crystallized lithium oleate by addition of dilute hydrochloric acid, extraction with ether, washing, evaporation of the solvent and drying *in vacuo*.

Anal. Calcd. for $C_{18}H_{34}O_2$: neut. equiv., 282.3; iodine no., 89.9. Found: neut. equiv., 283; iodine no., 89.5.

In order to characterize definitely the acid as oleic, it was converted into the *p*-phenylphenacyl ester.[12] This melted at 57.5–59° after three crystallizations while that from a sample of natural oleic acid purified through the lithium salt melted at 58.5–60° after two crystallizations. The mixed melting point was 58–59.5°.

The first crop of 20.1 g. of lead elaidate on recrystallization from 550 cc. of alcohol and 5 cc. of acetic acid gave 18.5 g. melting at 87–89°. On shaking with dilute nitric acid and ether, and evaporation of the solvent, the calculated amount of solid acid was obtained. After two crystallizations from 95% alcohol at 0°, it melted at 44°.

Anal. Calcd. for $C_{18}H_{34}O_2$: neut. equiv., 282.3; iodine no., 89.9. Found: neut. equiv., 282; iodine no., 89.6.

The mixed melting point with a sample of elaidic acid freshly prepared from natural oleic acid and melting also at 44° showed no depression.

Summary

Oleic and elaidic acids have been synthesized by a procedure which does not permit the formation of structural isomers and which should be of general use for the synthesis of unsaturated fatty acids.

[12] Drake and Bronitsky, This Journal, **52**, 3715 (1930).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Tautomerism of the Aminonaphthoquinones

BY LOUIS F. AND MARY FIESER

In continuation of our potentiometric study of the unstable oxido-reduction systems formed by the aminophenols and their primary oxidation products,[1] we have applied similar methods of investigation to a survey of the corresponding compounds in the naphthalene series. It was of particular interest to see if the potentiometric method would furnish any information regarding the possible tautomerism of the aminonaphthoquinones to hydroxynaphthoquinone-imines, and to apply to this problem the general theory regarding such tautomeric equilibria which was developed in an earlier paper.[2]

Nearly all of the possible di- and tri-substituted naphthalenes containing either hydroxyl or amino groups or both in the 1,2-, 1,4- or 1,2,4-positions have been investigated. The oxidants formed in the course of the electrometric titration of these substances represent in many cases quinone-imines or di-imines which are unknown in the solid state and which are quite sensitive to acid or alkaline hydrolysis, but they display for the most part considerable stability in neutral or weakly alkaline buffer solutions, particularly when the reductants used are of a high degree of purity. The oxidants from 2-amino-1-naphthol and 2,3-diamino-1-naphthol, however, proved to be too unstable to per-

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[1] Fieser, This Journal, **52**, 4915 (1930).

[2] Fieser, *ibid.*, **50**, 439 (1928).