New Type Reactions

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Abstract

Many products of the reactions of fats and fatty acids are being commercially exploited. There are, however, many other potential products derived from new or inadequately developed reactions. Some of these reactions, involving both the carboxyl and the fatty acid hydrocarbon chain, will be discussed. Emphasis will be placed on the latter and will include examples of substitution, addition, and elimination reactions. New knowledge relating to some of these reactions will be stressed.

Introduction

A VERY LARGE NUMBER of chemical reactions of fats and fatty acids have been described in the technical literature and many of these are being exploited commercially today. However, this does not mean that opportunities in this field have been exhausted. Fats and fatty acids provide a very attractive raw material for chemical modification and it is the purpose of this article to describe some reactions which are not commercial and which deserve further study. A comprehensive review of the chemistry of fatty acids is beyond the scope of the article.

Discussion

Reactions of fatty acids fall into two categories, those which involve the carboxyl group and those which involve the hydrocarbon chain; and, of course, combinations of the two. Over the years major emphasis has been placed on carboxyl-group reactions. Commercial products of such reactions include soaps, esters, fatty alcohols, the nitrogen-containing derivatives such as amides, amines, and quaternary ammonium salts, etc.

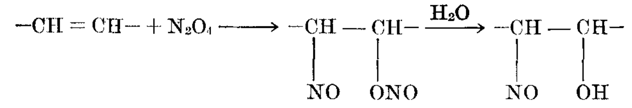
In recent years, reactions of the hydrocarbon chain of fatty acids have received an increasing amount of attention, and a number of commercial products and processes involve this type of chemistry. Among these are polymerization products derived from unsaturated fatty acids (including protective coatings produced from drying oils), products of oxidative cleavage, and epoxidized oils. Many other reactions of the fatty acid hydrocarbon chain are known, and some of these will be discussed in more detail. A review article which was published recently is recommended for those who may wish to pursue the subject more exhaustively (1). Information regarding the properties of the products to be discussed is frequently scanty; no attempt will be made to suggest uses for these materials.

Most reactions of the hydrocarbon chain of fatty acids fall into one of the following classes: replacement reactions, addition reactions, elimination reactions, or cleavage reactions. For the purposes of this discussion, it is convenient to follow this classification scheme.

Direct replacement by halogen of one or more hydrogens in the hydrocarbon chain of fatty acids offers many interesting possibilities which are discussed in another paper in this Symposium (2). Halogenated fatty acids may serve as intermediates for the introduction of other groups such as hydroxyl or alkoxyl (3,4,5,6), mercapto (7), amino (8,9), cyano (10), or dialkylphosphono (11).

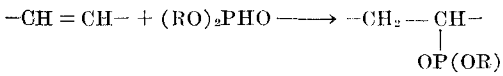
The addition of a large variety of reagents to the ethylenic linkage of unsaturated fatty acids has been reported in the literature. Some of these, such as hydrogenation, halogenation, and epoxidation are well known. Other perhaps less well known reactions will be described here. Although some of these involve relatively high-priced chemicals, it is always possible that properties of the product will justify a high cost.

Addition of N_2O_4 to unsaturated acids yields a nitrosonitrosoöxy acid which may be hydrolyzed to a nitrosohydroxy acid (12,13).



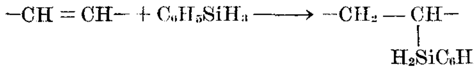
$$-CH=CH- + N_2O_4 \longrightarrow \underset{NO}{-CH}-\underset{ONO}{CH}- \xrightarrow{H_2O} \underset{NO}{-CH}-\underset{OH}{CH}-$$

(This reaction, and those which are discussed subsequently, yield mixtures of positional isomers, since addition is random.) Dialkylphosphonite will add to esters of monoölefinic acids to produce the dialkylphosphono derivative of the corresponding saturated acid (14).



$$-CH=CH- + (RO)_2PHO \longrightarrow -CH_2-\underset{OP(OR)_2}{CH}-$$

Addition of silane derivatives is illustrated by phenylsilane and a monoölefin (15).



$$-CH=CH- + C_6H_5SiH_3 \longrightarrow -CH_2-\underset{H_2SiC_6H_5}{CH}-$$

The last two addition reactions require a peroxide catalyst.

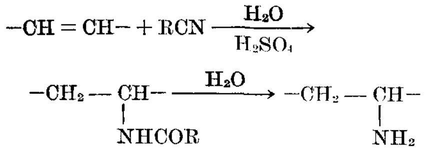
Hydroboration of internally unsaturated hydrocarbons followed by oxidation and hydrolysis leads to terminal alcohols.

$$CH_3(CH_2)_nCH=CH(CH_2)_mCH_3 + B_2H_6 \longrightarrow$$

$$\text{addition compound} \xrightarrow[\text{2. Hydrolyze}]{\text{1. Oxidize}} CH_3(CH_2)_{m+n+3}OH$$

When this series of reactions was carried out with methyl oleate, a mixture of 9- and 10-hydroxyoctadecanoic acids was obtained; no isomerization occurred (16). Subsequent work has shown that the isomerization of the diborane addition product is influenced by the terminal carboxylate group (17).

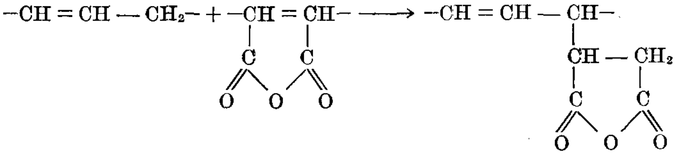
A number of addition reactions of olefinic fatty acids produce carbon-to-carbon bonds. Addition of nitriles yields amido acids which may be hydrolyzed to the amino acid (18).



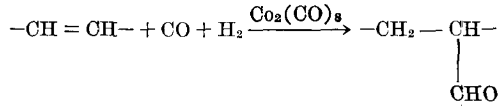
$$-CH=CH- + RCN \xrightarrow[H_2SO_4]{H_2O}$$

$$-CH_2-\underset{NHCOR}{CH}- \xrightarrow{H_2O} -CH_2-\underset{NH_2}{CH}-$$

The Friedel-Crafts reaction between aromatic compounds and olefinic acids will produce saturated acids with aromatic substituents (19). Aluminum chloride and other acidic catalysts are used. Addition of maleic anhydride to methyl oleate yields a mixture of adducts involving the 8-, 9-, 10-, and 11-carbon positions (20). This is a free radical reaction; one of the products may be illustrated by the following reaction.

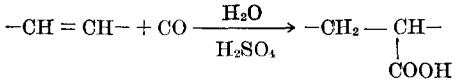


Other addition reactions which produce carbon-to-carbon bonds are the "oxo" process, involving the addition of carbon monoxide and hydrogen (21),



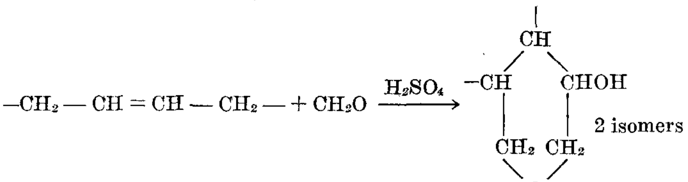
$$-CH=CH- + CO + H_2 \xrightarrow{Co_2(CO)_8} -CH_2-\underset{\displaystyle CHO}{CH}-$$

and the carboxylation of olefinic acids by means of carbon monoxide in strong acid (22).

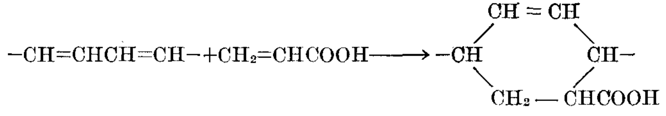


$$-CH=CH- + CO \xrightarrow[H_2SO_4]{H_2O} -CH_2-\underset{\displaystyle COOH}{CH}-$$

Formaldehyde will also add to unsaturated acids to yield a mixture of products (Prins reaction) (23).



Polyunsaturated fatty acids which are conjugated or are capable of undergoing conjugation are subject to the Diels-Alder reaction with a number of dienophiles (24). The chemistry involved may be illustrated by the reaction of a butadiene system with acrylic acid.

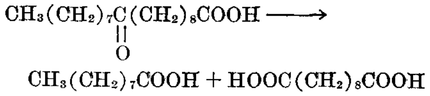


Conjugated trienoic acids, such as eleostearic (usually as the ester), are susceptible to cyclization when subjected to heat (25). Esters of linolenic acid also form cyclic monomers when heated with base (26). Dimerization reactions of dienoic fatty acids are well-known.

Addition reactions also include those which involve the interaction of epoxy fatty acids with various reagents such as hydrogen, water, alcohols, hydrogen halides, and amines. The chemistry of epoxides will be discussed in another paper in this Symposium (27).

Elimination reactions of fatty acids or their derivatives are usually undertaken as a means of introducing unsaturation into the molecule. Dehydration of ricinoleic acid is an example of such a reaction which is applied commercially today. Many reports in the literature describe attempts at dehydrogenation, dehydration, or dehydrohalogenation of saturated acids, hydroxy acids, or halogenated acids, respectively. With certain exceptions, these elimination reactions are, at best, only moderately successful. Many references describing elimination reactions are included in the review cited above (1).

Cleavage of the fatty acid hydrocarbon chain is accomplished by pyrolytic or chemical (usually oxidative) means. Pyrolysis of unsubstituted saturated fatty acids produces a variety of products and does not appear to be an attractive reaction (28). Alkali fusion of keto acids yields a mixture of mono- and dibasic acids. It is actually a combination of pyrolytic and oxidative cleavage. Thus, 10-oxoöctadecanoic acid yields as major products nonanoic and decanedioic acids (29).



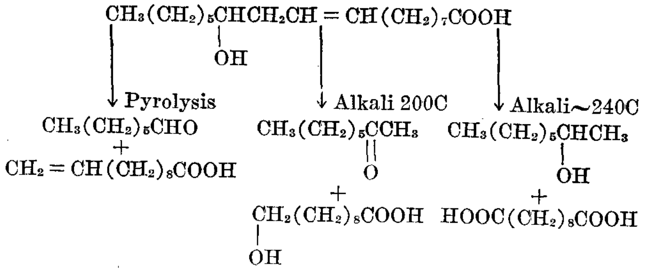
$$CH_3(CH_2)_7\underset{\displaystyle O}{\overset{}{C}}(CH_2)_8COOH \longrightarrow$$
$$CH_3(CH_2)_7COOH + HOOC(CH_2)_8COOH$$

Octane is also a product of this reaction, as are small amounts of other products. Alkali fusion of hydroxy acids yields similar results, since dehydrogenation to the keto acid occurs under the conditions of the reaction.

Pryolytic cleavage of unsaturated acids is best exemplified by the Varrentrapp reaction which was first described in 1840. This reaction, also an alkali fusion, is both pyrolytic and oxidative in character. The mechanism of the reaction has been elucidated recently (30,31). Under the conditions of reaction, the shift of the double bond in the unsaturated fatty acid occurs in both directions from the original position. Shifts into the 2-position are followed by irreversible fission. Ultimately, good yields of the saturated fatty acid containing two less carbon atoms than the original unsaturated acid are obtained. The end result of the reaction is as follows:

$$-CH=CH(CH_2)_nCH_2CH_2COOH \xrightarrow{Base}$$
$$-CH_2CH_2(CH_2)_nCH=CHCOOH \xrightarrow[H_2O]{Base}$$
$$-CH_2CH_2(CH_2)_nCOOH + CH_3COOH$$

Pyrolytic cleavage of ricinoleic acid is not a new reaction. In fact, it is used commercially for the production of both 10-undecenoic and sebacic acids. The course of the reaction which is dependent upon the conditions of the pyrolysis is as shown (32).



A scheme which accounts for the temperature dependence of the alkaline fusion has been proposed (29).

Oxidative cleavage by means of ozone is discussed elsewhere in this Symposium (34).

The reactions which have been discussed above by no means represent all of the possibilities which may interest those concerned with finding new products and new processes based upon fats or fatty acids as raw materials. Furthermore, it must be made clear that many of these reactions have not been developed to the point of commercial feasibility, nor are uses for the products necessarily known. Certainly, there are many unexploited opportunities for the chemical modification of fats and oils—diligence and imagination will be rewarded.

REFERENCES

1. Harwood, H. J., Chem. Revs., *62*, 99 (1962).
2. Sonntag, N. O. V., JAOCS, In Press.
3. Buu-Hoi, N. P., and P. Demerseman, J. Org. Chem., *18*, 649 (1953).
4. Guest, H. H., and C. M. Goddard, Jr., J. Am. Chem. Soc., *66*, 2074 (1944).
5. Guest, H. H., *Ibid.*, *69*, 300 (1947).
6. Paulshock, M., and C. M. Moser, *Ibid.*, *72*, 5073 (1950).
7. Mazonski, T., and S. Goszczynski, Zeszyty Nauk. Politech. Slask. Chem. No. 2, 27 (1957).
8. Elks, J., B. A. Hems, and B. E. Ryman, J. Chem. Soc., 1386 (1948).
9. Fieser, M., L. F. Fieser, E. Toromanoff, Y. Hirata, H. Heymann, M. Tefft, and S. Bhattacharya, J. Am. Chem. Soc., *78*, 2825 (1956).

10. Chicosine, A., G. Dupont, and R. Dulou, Bull. soc. chim. France, 1232 (1957).

11. Ackerman, B., R. M. Chaladek, and D. Swern, J. Am. Chem. Soc., *79*, 6524 (1957).

12. Vasil'ev, S. V., Trudy Moskov Inst. Tonkoĭ Khim. Tekhnol im M. V. Lamonosva, No. 5, 50 (1955).

13. Vasil'ev, S. V., Zhur. Obshcheĭ Khim., *26*, 712 (1956).

14. Sasin, R., W. F. Olszewski, J. R. Russell, and D. Swern, J. Am. Chem. Soc., *81*, 6276 (1959).

15. Speier, J. L., R. Zimmerman, J. Webster, *Ibid.*, *78*, 2278 (1956).

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

17. Logan, T. J., J. Org. Chem., 26, 3657 (1961).

18. Roe, E. T., and D. Swern, J. Am. Chem. Soc., *75*, 5479 (1953).

19. Stirton, A. J., B. B. Schaeffer, A. A. Stawitzke, J. K. Weil, and W. C. Ault, JAOCS, *25*, 365 (1948).

20. Bickford, W. G., G. S. Fisher, L. Kyame, and C. E. Swift, *Ibid.*, *25*, 1080 (1948).

21. Gresham, W. F., R. E. Brooks, and W. M. Bruner, U. S. Patent 2,437,600 (1948).

22. Roe, E. T., and D. Swern, JAOCS, *37*, 661 (1960).

23. Pigulevskiĭ, G. V., and M. G. Tatarskaya, Zhur. Obshcheĭ Khim, *20*, 456 (1950).

24. Teeter, H. M., J. L. O'Donnel, W. J. Schneider, L. E. Gast, and M. J. Danzig, J. Org. Chem., *22*, 512 (1957).

25. Paschke, R. F., and D. H. Wheeler, JAOCS, *32*, 473 (1955).

26. Scholfield, C. R., and J. C. Cowan, *Ibid.*, *36*, 631 (1959).

27. Findley, T. W., *Ibid.*, In Press.

28. Demorest, M., D. Mooberry, and J. D. Danforth, Ind. Eng. Chem., *43*, 2569 (1951).

29. Dythan, R. A., and B. C. L. Weedon, Tetrahedron, *8*, 246 (1960).

30. Ackman, R. G., P. Linstead, B. J. Wakefield, and B. C. L. Weedon, *Ibid.*, *8*, 239 (1960).

31. Lüttringhaus, A., and W. Reif, Ann. *618*, 221 (1958).

32. Hargreaves, G. H., and L. N. Owen, J. Chem. Soc., 753 (1947).

33. Maggiolo, A., and R. G. Kadesch, JAOCS, In Press.

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Hydrogenation of Fats and Oils. Isomerization During Hydrogenation[1]

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Abstract

This presentation includes a survey of the development of the presently accepted theory for the formation of isomers based on a half hydrogenation-dehydrogenation mechanism with atomic hydrogen, an appraisal of the relevant work of recent years for its significance when applied to the problem of isomerization, and certain experimental evidence from other fields of heterogeneous catalysis of interest in the hydrogenation of fats and oils. Effects of temperature, pressure, catalyst concentration, and degree of agitation used in commercial plants on the degree of isomerization are discussed. In addition the conditions necessary for the proper application of the term "selective" to a hydrogenation are examined. An interpretation of recent work to reduce isomerization while retaining selectivity by extending the normal range of the variables and by the use of solvents is covered. Selected works on catalysis from related fields are used to indicate possible modifications of the isomerization mechanism and, perhaps, to reveal fruitful avenues of research.

Introduction

HYDROGENATION is the oldest and most important of the commercial processes used in the chemical modification of fats and oils. Sabatier in France as early as 1897 and Normann in Britain in 1903 were responsible for the basic development of the process as it is known today. By 1911, the first commercial product containing hydrogenated fat was on the market in this country. Today, the importance of the process is difficult to overemphasize. Currently, in excess of three billion pounds of vegetable oils are hydrogenated annually. The process has contributed more than any other technique to the great increase in the diversity of use of various fats and oils.

Discussion

Essentially the process involves bringing together an unsaturated fat or oil, a nickel catalyst, and hydrogen under such conditions that the hydrogen combines with the oil. The product is usually a semi-solid, or plastic fat. The original purpose of this process was to permit the use of cheaper vagetable oils in the place of more expensive animal shortenings. The first commercial products were crude and, sometimes, unsatisfactory. They consisted of blends of a solid (completely hydrogenated) fat with a liquid (refined and bleached) oil. It was not unusual for the consumer of the early products to find that the two phases had separated into their original unblended state. There was some "consumer resistance." Gradual improvements in the process and the products led to today's all-hydrogenated shortenings and related products, that are not only accepted, but are preferred by many consumers.

Yet, even today, hydrogenation must be regarded as an enigma of the fat and oil industry. Fundamentally, it is not well understood. Certain problems, which have plagued the industry from the beginning, are growing in importance. Much can be done toward modifying and improving the hydrogenation of vegetable oils. An increasingly recognized problem is that these hydrogenated oils differ chemically from natural oils to a large extent. An excellent review of the changes in the nutritive value of fats and oils after hydrogenation is available (10). Hydrogenated oils contain glycerides that may consist partially of positional and geometric isomers of normal linoleic acid. Hydrogenated oils may contain large amounts of positional and geometric isomers of oleic acid, *cis*-9-octadecenoic acid. It is generally agreed that glycerides of these isomers of oleic acid are utilized by the animal body as readily as are those of oleic acid itself, provided the fat product in which they occur does not have too high a melting point. Further work may be needed to assess fully the importance of isomeric products in human diets.

While no solution to the problem of eliminating the formation of geometrical or positional isomers during hydrogenation will be presented, it is hoped that various sections of this discussion will be of value to those interested in this field. The objectives of this paper will be to survey the development of the presently accepted theory for the formation of isomers, to appraise some of the more relevant work of recent years for its significance, to stress the paucity of the means of solution with the present theory, and to engender interest in more fruitful avenues of research by reviewing certain work from other fields of heterogeneous catalysis.

Development of Theory

The historical evolution of present-day theory of

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[1] Presented at the AOCS meeting in New Orleans, 1962.