Straight-Chain Fatty Acids from Alcohols, Olefins, and Ziegler Intermediates

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Abstract

Six synthetic routes to straight-chain saturated fatty acids other than from saturated hydrocarbons currently in research and development within the petrochemical industry are discussed and evaluated and the prospects for each reviewed in the light of advantages and disadvantages for each.

Introduction

Oxidation of Straight-Chain Alcohols

The chemistry involved in the oxidation of aliphatic alcohols to aliphatic carboxylic acids has been known and fairly well understood for over 80 years. It should come as no surprise to any organic chemists in the audience that such a reaction is feasible, perhaps even commercially realistic. Certainly, we have been aware for a good many years that an intermediate product such as lauraldehyde, for example, could be readily prepared by the gentle dehydrogenation of lauryl alcohol, prepared, in turn, from lauric acid by catalytic reduction with copper chromite catalyst, or, perhaps, from methyl laurate by sodium reduction. The second step in the oxidation, a conversion of intermediate aldehyde to lauric acid, is a reasonably well-known laboratory chemical reaction, although over-all yields, catalyst performance, and minimization of losses by aldehyde polymerization and other reactions during this step are of some concern. Notwithstanding, this so-called classical route to straight-chain fatty acids is today occupying some not insignificant attention within the petrochemical industry. Recognizing that the second step in the over-all oxidation leaves something to be desired, the synthesis by this route must command attention within the industry, particularly to those segments which have available to them synthetic long-chain alcohols.

The alcohols to which we allude are, of course, Ziegler-process straight-chain alcohols. Economically, can a synthesis based upon these products as raw materials achieve any reasonable degree of commercial success? Three factors seem to indicate that it would be exceedingly difficult under today's economics and technology. First, Ziegler-process alcohols are relatively expensive raw materials to employ in oxidation to fatty acids. Consider that lauryl alcohol and stearyl alcohol, conservatively production-costed at about 20 and 16 cents per pound, respectively, can hardly be expected to be converted into 95% grades of lauric and stearic acids at today's tankcar prices of 27.75 and 20.45 cents per pound and provide petrochemical organizations the profit margins they are accustomed to. Second, it is highly unlikely that process improvements in Ziegler-process alcohol production will result in lower costs for alcohols that are significant in the near future. Finally, it is probably unlikely that innovations in two-step catalytic oxidations of alcohols to acids will be able to provide products at 3 to 5 cents per pound unit processing costs, despite the fact that we live in an age of technological miracles and each day brings surprising developments. In view of all this, it is really unlikely that synthetic fatty acids produced by the oxidation of long-chain alcohols will be commercial realities. If we are wrong in the basic assumptions we have made so far, the least that can be said for this synthesis is that it will be difficult to commercialize.

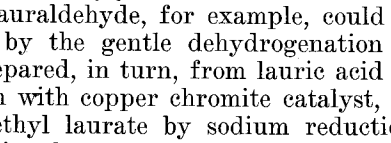

FIG. 1. Oxidation of straight-chain alcohols.

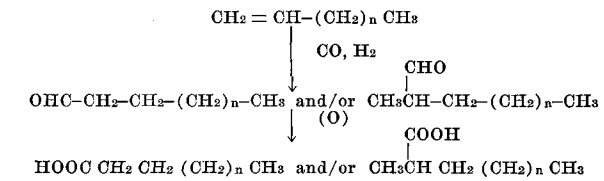

FIG. 2. Carbonylation of straight-chain terminal olefins.

Carbonylation of Straight-Chain Terminal Olefins

Those organizations within the petrochemical industry strong in "oxo-process" know-how are likely to be investigating the synthetic route outlined in Fig. 2. Actually, we have already pointed out that commercial products derived by this synthesis have already been introduced with limited success from raw material olefins which are branched-chain. The application of such oxo reactions to straight-chain olefins appears to offer considerably more potential, particularly in view of late technology developments.

Straight-chain terminal olefins are available as inexpensive raw materials, either by hydrocarbon cracking or by Ziegler-process technology, and when one considers that tankcar prices, not costs, of such potential raw materials range from 7¢ per pound for C 6–7 fractions to 12¢ per pound for C 15–20 mixtures, this synthetic route must merit very serious attention.

Those petrochemical organizations who have staked their success on Ziegler-process technology for terminal olefin production have the requisite straight-chain olefins available to them. Only fractional distillation is required to achieve the proper distribution of chain lengths that is required, a unit operation efficiently practiced by virtually all the members of the petrochemical industry. Those petrochemical organizations who produce their terminal olefins by hydrocarbon cracking technology undoubtedly have research effort underway on processing for the efficient separation of straight and branched-chain terminal olefins. Urea and thiourea adduct separations are no longer laboratory operations, and some development effort is being expended here, as well as on other methods of separation.

A large and sustained effort is undoubtedly being made to develop more effective processing for 1-addition of the carbon monoxide to terminal olefins, thus affording the 1-aldehyde rather than the branched chain isomer. Nor is a complete 1-addition required in this synthesis; there is still the good possibility that some improvement in the about 70/30 ratio of straight chain to branched chain products obtained can be translated into economic feasibility by a separation of branched from straight-chain acid products by

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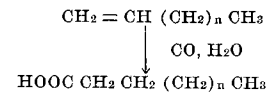

FIG. 3. Carboxylation of straight-chain terminal olefins.

a similar process used for olefin separation. This presumes, of course, that some use can be developed for the separated and recovered branched-chain isomeric acids. Obviously, there are still some problems to be solved in the oxidation of the oxo-process aldehyde intermediates to acids, but, all in all, this synthetic route is a real threat, both technically and economically, for the synthesis of straight-chain fatty acids. Conservative estimates indicate with little doubt that no less than four major research programs are currently underway on aspects of this synthetic fatty acids approach within the petrochemical industry.

Carboxylation of Straight-Chain Terminal Olefins

This synthetic route obviates the need for any troublesome oxidation step such as that required in carbonylation, but the advantage in this direction is somewhat offset by several other limitations. The carboxylation reaction is generally carried out in reaction media such as concentrated sulfuric acid, occasionally with acid catalysts like boron trifluoride adducts. These materials are, at best, difficult to handle in any equipment; in order to do so somewhat higher capital expense is likely to be encountered as corrosion rates are high and semi-hazardous operation, at least, is the price this synthesis demands for advantages such as simplicity, directness and relative freedom from the production of non-carboxylic by-products. Furthermore, the specificity for 1-addition in carboxylation, insofar as the limited data that are available for review indicate, is less than for carbonylation. Despite the limitations mentioned, this technology is of interest.

Curiously, carboxylation has been extensively developed through semi-works scale in Europe. In western Europe carboxylation of the olefin oleic acid affords a mixture of C-19 dibasic acid products [Koch, H., *Fette Seifen Anstrichmittel, 59,* 493–498 (1957)]; however, carboxylation for monobasic acids has, thus far, not been applied on a commercial scale.

Oxidation of Ziegler Intermediates

If the oxidation of Ziegler-process straight-chain alcohols is difficult to achieve economically, one must logically assume that oxidation of Ziegler intermediates would be investigated. After all, one would not consider the economical production of terminal olefins by dehydration of long-chain alcohols when olefins are much more efficiently prepared by disproportionation and pyrolysis of Ziegler intermediates. Can the self-same intermediates be oxidized to straight-chain fatty acids?

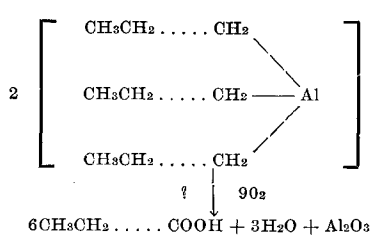

FIG. 4. Oxidation of Ziegler intermediates.

This synthetic approach is really the "dark horse" candidate. New, challenging, potentially-attractive, this synthesis cannot help but attract the imagination of synthetic organic chemists everywhere.

In the Ziegler synthesis of long-chain alcohols, one of the essential steps is a "gentle" air oxidation of trialkyl aluminums to aluminum alkoxides, just prior to a final hydrolysis of the alkoxides to alcohols. The challenge for fatty acid synthesis appears to consist of applying a more severe oxidation to the O-linked carbon atom in order to yield a carboxylic acid group without chain cleavage oxidations which would degrade the products. Can such a conversion be achieved economically, perhaps catalytically with air, perhaps with ozone, perhaps, even, with dilute nitric acid? All that can be said at this time is this: if it can be achieved technically, the oxidation step must be process-developed to have a unit cost less than 5¢ per pound in order for this synthetic route to be competitive.

If oxidations can be achieved economically, towards what markets can we expect the petrochemical industry to direct itself? In view of the availability of cheap, readily accessible tallow, one would not expect to see a petrochemical production from ethylene of palmitic or stearic acids in the near future. On the other hand, lauric acids of all kinds are consumed to the extent of about 26–27 million pounds and are derived from nondomestic coconut oil. Here is a more likely target. While the demand for lauric acid is presently satisfied by a range of acids from coco, hydrogenated coco, and 40%, 70%, 90%, and 95%-C-12 type lauric acids, this spectrum of products does not particularly lend itself to petrochemical marketing programs. Nevertheless, the prices of lauric acids ranging from 21½ to 23½ ¢/lb are attractive. Other target areas which are likely to be attracting considerable attention are the octanoic-decanoic family of fatty acids, ranging in price from 25½ to 27 ¢/lb, and the longer-chain fatty acids containing C-20 to C-24 homologs, ranging in price from 26 to 39 ¢/lb, which are expanding in volume.

Carboxylation of Ziegler Intermediates

While oxidation of ethylene-derived Ziegler intermediates without degradation is potentially capable of economic production of synthetic straight-chain fatty acids containing an even number of carbon atoms, the synthesis involving carboxylation is capable of the production of synthetic straight-chain fatty acids containing an odd number of carbon atoms.

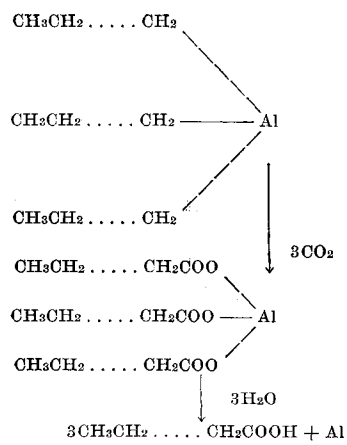

FIG. 5. Carboxylation of Ziegler intermediates.

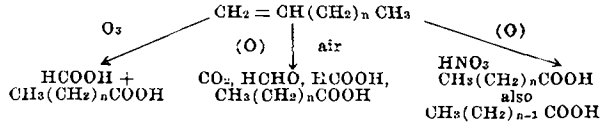

FIG. 6. Oxidation of straight-chain terminal olefins.

Our fatty acid-nourished economy has, thus far, been based upon even numbered carbon acids and derivatives which occur in and are derived from natural fats and oils. Can we be sure that long-chain fatty acids of odd number carbon chain length will not be equally suited for a majority of these applications, and perhaps, even better suited for a variety of new ones?

Oxidation of Straight-Chain Terminal Olefins

Three factors appear to have limited the ozonization of straight-chain terminal olefins to synthetic fatty acids: the present cost of ozone and its generation at about 12 ¢/lb, the difficulties and hazards of operating such processing, and the disposal of formic acid by-product. Typical of the American petroleum industry's attempts to use cheap and readily available air or perhaps oxygen as the oxidative reagent is Standard of Indiana's catalytic oxidation of straight-chain olefins to synthetic fatty acids with molecular oxygen in the presence of bromine and heavy metal catalysts [Jason, E. F., and E. K. Fields (Standard Oil Co.) U.S. Pat. 3,076,842 (Feb. 5, 1963)]. The process may be too corrosive for normal materials of construction to be feasible for production. Nitric acid oxidation is always a possibility for synthetic fatty acids from these raw materials if chain degradation can be minimized and the formation of extensive quantities of nitro compounds can be avoided as undesirable byproducts, or, on the other hand, if adequate separative technology can be developed to economically purify the major products.

Before concluding, I wish to dispel the possible impression that the members of the natural fatty acids group of this seminar possess all the research secrets on synthesis of fatty acids that are held within the petrochemical industry. Obviously, more research is being carried out than we are privileged to be aware of, this will continue to be the case in the future. Many byproduct streams are being examined with renewed interest. Security obviously prevents disclosures of intent on the part of much of the petrochemical industry; the bulk of the work underway is in the research stage, and it is still early for extensive large scale pilot plant construction. But the future is just around the corner, and it well behooves the natural fatty acid industry to make itself aware of the breadth and magnitude of the threat and to formulate its defensive tactics.

DR. RUTKOWSKI: The aluminum alkyls have been very dear to my heart, since I have done some work on them myself in the past. I wonder whether you would hazard a comment on whether the industry is close to achieving a one-step oxidation of Ziegler trialkyl aluminums to fatty acids economically?

DR. SONNTAG: Well, I'm on a spot if I've ever seen one. I don't really know; I'm not with a petrochemical research organization, but if I have to guess, I'd have to put my money on the carboxylation of the Ziegler intermediates. I personally don't think that they can be oxidized vigorously without losing yield due to degradation. Of course, tomorrow's Patent Gazette may prove how very wrong I am about this. I really don't think we will see an economical synthesis by oxidation of Ziegler intermediates in the next five years, if at all. On the other hand, with respect to carboxylation, I'd be a little worried about this, and I wouldn't want to guess about how quickly this development might materialize. It could be a lot faster than most of us realize.

DR. RUTKOWSKI: I think I would agree with you there.

DR. ZILCH: Dr. Sonntag, I just wondered whether you have found, along these synthetic lines, that unsaturated straight-chain fatty acids might be synthesized by any of these methods?

DR. SONNTAG: Yes, this probably is going to happen, sooner or later. The obvious approach is to copolymerize ethylene with a little acetylene here and there, or other triple bond monomers, to get a random distribution of unsaturated long-chain character. It is just a matter of time. If the petrochemical industry is successful in the economical synthesis of long-chain saturated fatty acids, it will not be long before they can create acids with unsaturation. There is also the possibility that they can synthesize the saturated products cheaply, and then dehydrogenate. This has already been done with methyl stearate to a mixture of isomeric methyl oleates [Margaillan, L., and X. Angeli, *Compt. rend., 206,* 1662–1663 (1938)] or with oleic acid, as the case may be, as long as 30 years ago. So, I think, perhaps, that we had better watch the possibility, that if saturated chains in synthetic acids are economically feasible, we had better be alert to the possibility of dehydrogenation for the unsaturated acids, rather than by direct synthesis. After all, Mother Nature put the 9, 12, and 15 systems of double bonds in natural fats, but who can say that other synthetic arrangements of unsaturation will not provide us with better alkyd resins or drying oils?

DR. ZILCH: Even fermentation methods may be developed to dehydrogenate saturated fatty acids.

DR. SONNTAG: Gentlemen, we have covered fairly well three aspects of the general problem. Now let us focus on the last aspect of this subject. What about the prospects for the direct synthesis of fatty acid derivatives from petrochemical basestocks? We have Richard Reck from Armour with us, and he will talk about what Armour has done in this general area. I suppose that some of the natural fatty acid producers may sit back and say that it cannot happen, but here is a presentation from one natural fatty acid and derivative producer who is doing something in petrochemical synthesis.

New Technology Involving Nonfatty Basestocks at Armour

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Abstract

Use of nonfatty raw materials for the production of a variety of new aliphatic chemical derivatives are discussed, including petroleum-derived olefins, which are converted by Armour Industrial Chemical Co. to so-called "β-Amines."