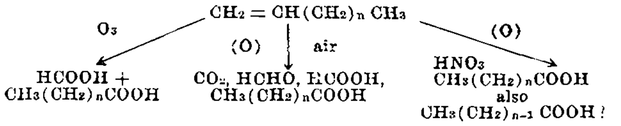

FIG. 6. Oxidation of straight-chain terminal olefins.

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 byproduct. 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

RICHARD A. RECK, Armour Industrial Chemical Company, Chicago, Illinois

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."

Introduction

In order to understand our position in the petrochemical derivative business, it would probably be best for me to do a little reviewing. Armour got into the fatty acid derivative business about thirty years ago for the purpose of starting something new and to make profits. In the early 30's, Armour had available to it real low cost fat supplies, and fatty acids. When I say low cost raw materials I do not mean the 5–9 cent/pound materials that we discussed earlier today, but, rather, raw materials of good quality available at 2–3 cents/pound, and, in some cases, even lower than that. The Armour management decided that this was a situation that something had to be done about.

Accordingly, a group of fat chemical scientists and engineers was put to work, first in the laboratory, then in the pilot plant, then in semi-works scale, on a series of fatty acid nitrogen derivatives, the so-called "upgraded" fatty acids. About the middle 30's, Armour built its first fatty nitrile/fatty amine plant. It was by present standards, a relatively small plant, but from it came, eventually, many products, in fact, more products than there were, in all cases, uses and markets. The first use area was the ore flotation field. It was not large at the start, and it is much bigger now, of course.

The first plant was versatile and was adaptable for the production of a variety of nitrogen derivatives. A real need was satisfied through the organization of an applications laboratory to go along with the synthetic program and the process development program. Uses were created for these new fat chemicals, and anyone who is familiar with the nitrogen derivative business can locate the Armour use patents which resulted from this part of the effort. Collectively, a rather healthy program was started in this way, and proved to be attractive to us for 15–20 years. In 1948–50, or thereabouts, one or two competitors entered the field, and there appeared, for the first time, a degree of overcapacity for fatty nitrogen chemicals. Faced with this situation, Armour could have taken several different courses of action. Cutbacks could have been made in basic research, or in use/applications work, or technical service, prices could have been lowered, or, on the other hand, new market development work could have been initiated, along with better technical service to the several customer industries, in order to stimulate the markets. Armour chose the latter. Ever since that time we have continued to maintain a large research staff on both nitrogen derivatives and esters.

We did not consciously limit ourselves to only one type of feedstock in our derivative program. We were always familiar with animal fats and the fatty acids derived therefrom, so, naturally, the bulk of our production was based on utilization of this raw material. Vegetable oils were used whenever the fatty acids required were to be found only from them, and, also, when more economically advantageous. Lately, we have undertaken a program to utilize petrochemical basestocks for our chemical production. The research and development work was started some years ago, and we are just now beginning to see the translation to commercial practice. We are planning the construction of a new plant for the manufacture of amine derivatives which employs petrochemical raw materials exclusively. I would like to review with you today some of the work that was done, and is still being done at Armour with petrochemical basestocks.

One of the earliest approaches is typified by U.S. patent 3,076,044, which discloses an attempt by Armour to utilize Ziegler chemistry to produce alkyl chlorides from aluminum trialkyls in turn prepared from ethylene. The alkyl chlorides are useful in the derivative business; there does not appear to be any large market for alkyl chlorides as such, but these could have some value as intermediates. We do not plan, at the present time, to market alkyl chlorides, but should a need for these products develop, as a final endproduct or as an intermediate, the technology is available in our storehouse of knowledge. The work could be expanded easily, and more development work could be directed to this, should it be desirable. The yields of alkyl chlorides are good, they are not excellent, but improvements could be made.

A different kind of development is outlined in our U.S. patent 3,083,218. This is part of a process for the production of secondary alcohols through the use of aluminum alcoholates, or alkoxides, as they are also called. Aluminum alkoxides, reacted with ketones, afford secondary alcohols. Of course, the alkoxides could be prepared by the oxidation of trialkyl aluminums prepared from ethylene, but our patent deals with a direct method for the preparation of the low molecular weight homologs by direct reaction of alcohols and aluminum in the presence of certain catalysts.

We do not, at this time, expect to produce secondary alcohols commercially, but here is a different kind of route for them in the event that we would need them. Incidentally, we have pilot plant production for a wide variety of fatty ketones, but this is not a petrochemical process. This is a patented, catalytic, vapor-phase, continuous process based upon the use of fatty acid or mixed fatty acid feeds. We produce several ketones as articles of commerce right now, and the possibilities for further chemical modification with these fat chemicals is quite large.

I hinted that we are using petrochemical olefins for nitrogen derivative production, but I want to point out that our U.S. patent 3,109,040 allows us to prepare α-olefins from fatty acids, which is really reversing the situation. This gives us a large measure of versatility in our operations. If olefins are ever high priced, which appears to be unlikely at the moment, or a certain fraction of feedstock olefin is unavailable, here is a route for the production of them from fats which could be employed. In this technology we take advantage of the homogeneous thermal catalysis of anhydrides to olefins. The anhydride chosen can be saturated or unsaturated. Can terminal olefins be produced with multiple systems of double bonds? Yes, they can, for we have found that oleic acid, through oleic anhydride, is converted into a diolefin with terminal unsaturation and with unsaturation in the center of the chain. We are not using this technology at the present time, either, but I think you can begin to appreciate some of the long range planning we are putting into this program.

We are producing amines from olefins and they are petroleum-derived olefins. These amine products have been researched and developed for more than two years, a pilot plant is currently in operation, a semi-works unit is in construction, and Armour will be in full production in 1967 or sooner. We have done the most obvious thing in producing the products from the olefins which are currently most available. We have a series of four primary amines, we call them β-amines to differentiate them from fatty compounds where the functional group is at the terminal position of the chain. The large bulk of the nitrogen functional groups in these new compounds are located at the β-position of the chain, which is, of course, the second carbon from the end. They are called Armeen L-7, derived from C-7 type olefin feedstock, Armeen L-9, from C-9 feed, Armeen L-11 from C-11 to C-15 feed, and Armeen L-15, from C-15 to C-20 feedstocks. These products are unique; they are different from fatty amines of the conventional type. Those of you who are familiar with saturated straight-chain amines will know that our dodecylamine, when pure, shows a melting point of 31.5C, and is sometimes a problem in winter storage. Armeen L-11, with roughly the same amine value or neutral equivalent, melts at −20F. Since these are new products we are undertaking new product development and market research effort on them, and we are enthusiastic. They are already far out of the laboratory curiosity stage.

In addition to the four primary amines, there are two diamines which are roughly comparable to those of our old "Duomeen" series. These are alkyl 1,3-propanediamines, and they are prepared by the addition of the "L"-type amines to acrylonitrile followed by hydrogenation to the primary/secondary diamine in the usual manner. We have already found a number of interesting applications for these products as a consequence of their different properties. The surface active properties of the new diamines are going to be quite different from those of the conventional straight-chain diamines. For example, Duomeen 12, a standard product, melts at 32C, but Duomeen L-11 exhibits a melting point of −32F. Obviously, these new diamines can satisfy some low temperature applications not satisfied by the older products.

In addition to the four primary amines and the two diamines, products may be prepared by taking advantage of any of the processing technology we have been using for years. I am talking about further modification of these amines by the ethoxylation, quaternization or salt formation methods to other derivatives. In due time these will probably be making their appearance.

These are a few of the things we have been doing at Armour. We will continue to take advantage of any kinds of raw materials, and, also, any kinds of technology that appear to be useful. We also believe that it is well to start early on new approaches.

Dr. Sonntag: I should like to add one more thing to what Mr. Reck has already said. I have in my hand a U.S. patent [Tucker, N. B., and P. W. Ifland (Procter & Gamble Co.) U.S. Pat. 3,231,618 Jan. 25, 1966] assigned to a very large domestic detergent producer located in Cincinnati, Ohio. The company would be considered as both a producer and a consumer of natural fatty acids. The patent discloses a direct synthesis of tertiary amines from trialkyl aluminums. A second patent [Gwynn, B. H., and A. C. Whitaker (Gulf Research and Development Co.) U.S. Pat. 3,080,424 (March 5, 1963)] issued quite recently to one of the very largest petroleum organizations in the United States reveals a process for the production of mixed primary and secondary fatty amines involving reacting aluminum alkoxides with ammonia, and this is even simpler than the first one. So, the answer to the question as to whether it is possible or realistic to synthesize derivatives directly from petrochemical basestocks is "yes." Only time will tell which ones we will see as commercial realities.

Gentlemen, we have come to the end of our allotted time. I suggest, that if there are any questions, some of us may be contacted in the halls. Thank you very much for your patience during this program. Our very sincere thanks to the individuals who participated in our discussion today and the organizations who permitted us to talk for them and about them. I declare this afternoon's program adjourned.