PANEL DISCUSSION AND SYMPOSIUM: SYNTHETIC FATTY ACIDS: A THREAT TO THE NATURAL FATTY CHEMICAL INDUSTRY?

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Introduction

DR. SONNTAG: The American Oil Chemists' Society National Program and Planning Committee and the Los Angeles Section welcome you to the first-of-a-kind panel discussion and symposium on the timely subject, "Synthetic Fatty Acids—A Threat to the Natural Fatty Chemical Industry?"

The seminar will attempt to cover by panel discussion and papers-within-the-seminar the preparation, properties, applications and market potentials of 1) synthetic carboxylic acids of the "neo" type, 2) synthetic branched-chain carboxylic acids, and 3) synthetic straight-chain saturated (and unsaturated) fatty acids. Specifically, we will treat the chemistry, production, properties, and applications of Enjay Chemical Company's "Neo-Acids" and the "oxo-process" branched-chain acids, present an up-to-date review of European synthetic fatty acids by oxidation of paraffinic hydrocarbons, discuss and analyze the prospects for synthetic straight-chain saturated and unsaturated fatty acids from olefins, alcohols, and Ziegler intermediates, and examine what one big natural fatty acid producer is doing with "petro-chemical-like" technology.

Permit me to introduce the participating panel members of our group today. Seated on my extreme right, your left, A. J. Rutkowski of Enjay Chemical Laboratories of Linden, New Jersey. Dr. Rutkowski is involved in the technical aspects of "Neo-Acids," and he speaks, obviously, from the petrochemical point of view. Next, Morton Fefer of Enjay Chemical Company, New York. Dr. Fefer is concerned and has a function at Enjay with new product development; among the new products, of course, "Neo-Acids" are prominent. On the other side of the central table is Karl T. Zilch of Emery Industries, Inc., of Cincinnati, no stranger to many of you in the fatty acid industry. Dr. Zilch has been active in research on natural fatty acids for many years. Next to Dr. Zilch Richard A. Reck of Armour Industrial Chemical Company, Chicago. Mr. Reck's function at Armour is primarily concerned with fatty acid derivatives, although I suspect that he has cut his teeth in the fatty acid area also. Finally, permit me to introduce myself, Norman Sonntag of Research and Development Division, National Dairy Products Corporation at Glenview, Illinois. If you are wondering what interest a dairy and food organization like ours has in this subject, let me explain that among our operating divisions is the Humko Products Division of Memphis, Tennessee, a natural fatty acids producer, and a producer of nitrogen derivatives and methyl esters.

Today, we do not wish to speak with overbearing assurance of complete authority. We wish to point out general trends, but without taking an individual company's position with respect to research trends within our organizations. We are not going to talk about our own marketing strategies or about any research planning within the laboratories of our respective companies. We feel free, however, to guess quite freely about everybody else's plans. I would ask that you refrain from asking questions; we have a good deal of subject matter to cover. I think, however, that if you meet any of these gentlemen outside in the halls, they will probably answer everything you want to know.

In attacking our subject, I think it best to start with an examination of the magnitude of the fatty acid industry. Concerning ourselves with fatty acids, and later with fatty acid derivatives, we would like to start this off by asking Karl Zilch to point out for us the magnitude in tonnage and in dollar sales of the fatty acid segment of the industry, defining it as a target at which petrochemical companies may make some effort in the future.

DR. ZILCH: The Fatty Acid Producers' Council, which represents the Fatty Acid Industry, reports an annual domestic production of approximately 900 million pounds. In dollar value this would be in the neighborhood of 100 million dollars. As you might expect, this poundage represents quite a broad spectrum of different fatty acid products. Because of the variable fatty acid composition of natural fats and oils from which these acids are derived as well

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as chemical modifications that can be brought about by the manufacturer himself, various types of fatty acids can be derived to satisfy the market needs.

Fatty acids from natural sources are generally classified as saturated and unsaturated acids with varying chain length between C_6 and C_{22}. In the 900 million pounds are included saturated acids falling within a chain length range of C_6–C_{22}, monounsaturates having a chain length range of C_{14}–C_{22} and polyunsaturates ranging from C_{18}–C_{22}.

Methods of processing fatty acids throughout the industry will vary between manufacturers which impart flexibility as to what the industry can produce. Common saturated and unsaturated fatty acids can vary in stearic acid composition between about 3 to 95%. This allows users of these products to choose a particular fatty acid for a specific end use application. As an example, Table I shows the different fatty acids which may be isolated from cottonseed oil and how through hydrogenation they can be converted into palmitic acid and stearic acid. In the hydrogenated cottonseed oil fatty acid product the percentage of unsaturates is nil. The 73% stearic acid content of the hydrogenated product could be increased to 95% by fractional distillation. The point I want to emphasize is that the 900 million pounds represents a variety of fatty acids which offers the consumer a wide selection of products to satisfy his particular end use application.

DR. SONNTAG: Thank you. Now, Richard A. Reck will provide a similar treatment for the fatty acid derivative segment of the industry.

MR. RECK: We can talk about many mixtures of different types of fatty acids, but in discussing derivatives, this number can be multiplied by a factor of "x" for the number of derivatives that can be made out of each fatty acid. Of course, we at Armour are most familiar with the nitrogen derivatives, and we start with nitriles and primary amines. But amines can be of many types: primary, secondary, tertiary, also certain types produced directly from fatty acids without the necessity for going through nitrile intermediates, such as imidazolines. We estimate—and it is only an estimate—that there are about 1 billion pounds of total derivatives produced and sold in the United States today. Now besides amines, we can include amine oxides (quite important commercially these days), amine salts, quaternaries, diamines, triamines, amides, polyamides (both reactive and nonreactive), alkyl halides, esters (industrial, cosmetic and food esters of the emulsifier type) and a few other types. When we say that there is today a 200-million-dollar market for assorted fatty acid derivatives, we are including many, many types; breaking them down and classifying them is anyone's problem.

DR. SONNTAG: You say about 200 million dollars sales for all sorts of derivatives representing perhaps approximately 1 billion pounds of production, and Dr. Zilch, your figure was perhaps 100 million dollars in sales representing about 870–900 million pounds of production for the fatty acids. Now, obviously there is a little discrepancy in these figures, due probably to the fact that included in the derivative figure is some production directly from fats and oils and not through fatty acids; nevertheless, they appear to be realistic. At any rate, this is quite a target and a challenge for petrochemical manufacturers. Let us go back for a moment and take a look at some of the advantages which the natural fatty acid industry and also the natural products themselves have. I should like to ask Dr. Zilch again: Just what are the advantages which the natural fatty acid industry has, and what has been built up over the last 15 to 25 years for these natural products?

TABLE I

	CSO fatty acids	Hyd. CSO fatty acids
C_{16}	26.0%	27.0%
$C_{16:1}$	1.0	...
C_{18}	3.0	73.0
$C_{18:1}$	17.5	......
$C_{18:2}$	51.0	......
$C_{18:3}$	0.5	......

DR. ZILCH: I think there are several advantages now, but perhaps some time later I may have to revise my thinking. At any rate, as we see it today there are a number of advantages to naturally derived fatty acids. One advantage is the replenishable supply of raw materials. If you examine the records over the past years, you will see that the production of fats and oils has been steadily increasing. There have been some spot fluctuations in the availability of certain raw materials which were caused mostly by adverse climatic conditions, government crop support programs or government export programs. With improvements in farming practices both in the United States and foreign lands as well as conversion of more land into crop production, there should be an increasing supply of fats and oils in the future.

Secondly, the manufacture of fatty acids from natural fats and oils can shift from one raw material to another and produce the same type of fatty acid. As you know, most manufacturers of fatty acids may use three or more natural fats and oils, depending upon their manufacturing processes and the type of finished goods they are interested in producing. The reason they can use these different raw materials is that the fatty acid components are identical. For example, if a manufacturer is interested in producing palmitic acid, he might use cottonseed oil, tallow, palm oil or lard oil as his raw material. Similarly linoleic acid can be derived from soybean oil, cottonseed oil, safflower oil, or sunflower seed oil. This means that if any fat or oil is in short supply he can change to another. This versatility also allows him to market fatty acids meeting edible, inedible or kosher requirements.

A third advantage is that the different manufacturers of fatty acids utilize the same raw materials and, therefore, market similar products. This allows the consumer to purchase acids from more than one supplier which gives him assurance of an uninterrupted flow of raw materials into his plant. As I will point out a little later in this program, synthetic fatty acids derived through oxidation of paraffinic hydrocarbons can have a considerable variation in composition depending upon the conditions employed throughout the process.

Another advantage is that over the years the consumer has been assured of uniform quality since a number of fatty acid products are manufactured throughout the industry within narrow specifications. Various people have commented that synthetic fatty acids, although not identical to natural fatty acids, could be utilized to produce similar products. This is true, but laboratory and market evaluations are time-consuming and costly. Only if the synthetic fatty acid can offer him an economic or performance advantage will he make a change.

An advantage to the manufacturer of natural fatty acids is that approximately 10% of the raw material is glycerine. Profits can be realized from the sale of glycerine which obviously affects the selling price of the fatty acids. Presently glycerine is being marketed at approximately 21 to 23 cents per pound.

The last advantage I want to mention is that natural fatty acids can be manufactured from relatively inexpensive raw materials such as tallow, cottonseed soapstock, tall oil, coconut oil soapstock, soybean oil soapstock, lard oil, etc.

Dr. Sonntag: A great many points have been made, and I should like to summarize a few of them. One was that the raw materials are self-replenishing, and a second was that they are plentiful and inexpensive, perhaps more so than most people realize. The fatty acid products now have good color, little odor, are consistent and are produced to meaningful specifications. I might add, in addition to what has been said, that the natural fatty acid industry has the FDA on its side, at least for food-additive uses. The cosmetic industry and the pharmaceutical industry have now learned to expect products with excellent color, low odor, fine texture and consistent quality. This, I suppose, must be an advantage. But, Mr. Reck, what can you add to clarify the picture in regard to the overall advantages now available to the natural fatty acid industry?

Mr. Reck: It is true that the fatty raw material picture is quite good. Through research, technical service, application research and process improvement, fatty acid producers have been able to improve their business over the last 15 years, while successfully shifting their feedstocks in so doing. For example, improved separation techniques have allow us to produce very high purity palmitic and stearic acids. It is also possible now to separate unsaturated acids such as oleic and linoleic acids by means of solvent crystallization. The advent of synthetic detergents has really increased the supply of fatty acids from tallow for other uses. The large availability of raw materials has led to a shift in the types of feedstocks which are in use today. Furthermore the fatty acid and fatty acid derivative producers have maintained large applications laboratories and have continued to come up with new uses for their products. Frequently the fatty acid producer works with a particular customer towards one end use, and while Dr. Zilch says that customers are interested in more than one supplier, generally the small customers are loyal to one supplier. If the producer can supply fatty acid that does the job for him, working through his own research and development people, it is possible to maintain that customer and most of his business for a considerable length of time. As I mentioned earlier, most of the fatty acid producers have developed through research or bought into a derivative line of products from fatty acids. Most notable in our industry are, of course, the nitrogen and ester derivatives. Having a large supply of raw materials from natural fats and oils such as tallow, soybean oil and coconut oil, gives a low-cost, steady base position. Our fatty nitrogen business is based upon the availability of a large supply of tallow as well as coconut oil. We do not consciously try to limit ourselves to these materials; we take advantage of shifts in economies and availability of other raw materials, and by maintaining a well-staffed applications and development laboratory and an "end-use" laboratory, we can shift our feeds and emerge in an advantageous position. We have not minimized basic research, but we have emphasized "end-use" research to try to develop more markets for these materials. In general, having a large selection of raw materials and shifting among them provides flexiblity which is a distinct advantage.

Frequently, in working with a derivative or with a customer, you will develop for him a product that has a tailored property such as color, lack of odor, "feel," melting point, etc., that he wants or needs. By working with him you can maintain your level of business.

Dr. Sonntag: I think your points are worth highlighting. You said something about the C-16 and C-18 natural fatty acids picking up the slack in the over-all use of tallow because soap has gradually been replaced by synthetic detergents. You said, in effect, that the fatty acid industry today is a "customer-oriented" industry. While you did not say it, I believe you intended to point out that it can range from a "one-drum-a-month" business to a huge operation of "tank-cars-a-day." And, of course, that is just the kind of situation it is. This may be an advantage in some cases, and it may be a disadvantage in others. You mentioned that most, but not all, of the fatty acid producers have a derivative line of products. This gives them a sound basic raw material position and that has to be advantageous.

Now let us look at the other side of the coin. Let's look at the petrochemical industry and see what its strong points are in the possible synthesis of fatty acids, or for that matter, any kinds of carboxylic acids. Dr. Fefer, what do you see as the basic advantages of the petrochemical approach to the synthesis of carboxylic acids?

Dr. Fefer: Two basic advantages of the petrochemical approach are availability of a wide variety of unsaturated intermediates and several types of technological routes for the conversion of these raw materials into carboxylic acids. From the raw material point of view the petrochemical manufacturer has certain built-in advantages. There is a series of mixed streams of olefins captively available to him, some pure, some not, which can be used for further conversion to acids by some oxidative route. He also has the possibility of starting with ethylene and producing a regulated molecular weight distribution or a "smear" of products. Once the streams are available from the refinery, the decision remains, which to use, and the technology best suited to make the desired acid. Most of the olefin technology is oxidative, e.g., nitric acid or ozone. Conventional "oxo"-type synthesis is another, and a fourth is an approach I should like to dwell upon in more detail later and is the one we at Enjay have already taken, namely, the "Neo-Acid" synthesis from olefins. I think that with this versatility the petrochemical manufacturer must select which route is best for him. He needs to look at what is available, what he wants to make, how to do it economically with his process "petrochemical style," where he will market it, and what price he will get.

I mentioned a moment ago that ethylene is a basic raw material for the petrochemical approach; it has a number of excellent possibilities for acid synthesis. I think it would be worthwhile, now, for Dr. Rutkowski to discuss the current status of ethylene production—where it is going and what its short and long-term prospects are.

Dr. Rutkowski: I think we all recognize that ethylene is probably one of the most important raw material feedstocks needed for the eventual manufacture of synthetic fatty acids. The ethylene industry is certainly a dynamic one, and the changes that are occurring within it are taking place at an ever-increasing rate. There are several important changes that are occurring now. Perhaps the most important is the increase in capacity and consumption, which is enormous. I think it interesting to note that within the past five years the consumption of ethylene for all kinds of chemicals has increased 60% or more. In western Europe there are currently about 9 billion pounds of ethylene produced. This is expected to increase to about 21.7 billion pounds by the end of 1967; this is more than double the present rate over less than two years. Predictions for the United States are that the Gulf Coast will almost double its capacity to about 13 billion pounds per year in 1970 from the present capacity of 6.9 billion pounds this year. In addition to this change, there is the big increase in the size of the plants which are producing ethylene. In the United States, where 200–300 million pound plants were once considered standard size, today the manufacturer of ethylene will not consider anything less than a plant sized for 300 million pounds, and it is more likely that 500 million pound plants will become standard size. There is even talk of a 1 billion pound a year plant for the United States. In Europe the increase in the size of the individual plants is even more dramatic. We thought in terms of standard plant sizes of about 50–100 million pound capacity, but today, most European producers are thinking in terms of standard plants of not less than 300 million pounds, several are presently considering plants at larger than 600 million pounds, and one company, in particular, is reported to have ordered a plant with a capacity of 1 billion pounds of ethylene.

A change which is occurring in favor of the small-volume consumer of ethylene is the method of supplying ethylene. The conventional distribution technique for supplying ethylene, is, of course, by pipeline, which furnishes ethylene vapor. This is a cheap distribution method, provided the ultimate consumer is a large-volume user. However, for chemical manufacturers who are either too far from pipelines, or consume insufficient quantities to justify pipeline supply, liquid ethylene is now available by means of insulated trailers. There are several organizations which are investigating this means of supplying ethylene. Enjay is one of them. Since 1959, Enjay has transported over 100 million pounds of liquid ethylene by trailer trucks. In one case, the transfer was over 1600 miles of highway.

Regarding the prices for ethylene, I believe that, as with prices of most other materials in the petrochemical industry, these have continued to go down, just in inverse proportion to the standard of living, which continues to go up. In 1960 on the Gulf Coast, ethylene was available at about 5¼ c/lb; the current price on the Gulf Coast is about 4c, and on the East United States Coast about 5 c/lb. In Europe, the prices fluctuate between 4–6 c/lb. These prices have declined even in the face of reasonably tight supply situations. In the United States the ethylene supply should be tight for the remainder of 1966, and possibly even to the end of 1967. This should ease up by 1968 with the projected capacity of new and expanded plants on-stream. Definitely, the tight supply of ethylene will affect the expansion of certain chemicals derived from it: polyethylene, ethylene oxide, ethylene glycol, etc. To emphasize the importance of ethylene to the petrochemical industry, in general, I should point out that in 1964 over 8 billion pounds of ethylene was consumed for the manufacture of 13 billion pounds of assorted petrochemicals: polyethylene, ethylene oxide, ethylene glycol, ethyl benzene for styrene, synthetic ethanol. The present uses of ethylene are large, and the opportunity for the use of ethylene in the manufacture of synthetic fatty acids is always present.

One of the basic advantages which the petrochemical industry has over the natural fatty acid industry is the ability to fractionally distill at large volume economies. This is, perhaps, not the case with the fatty acid industry. Dr. Fefer, what do you think about this?

DR. FEFER: Of course, that is one of the industry's technological strong points which will result in a lower-priced acid in the long run. But, in reference to your point on ethylene as a raw material, as more research is carried out we are probably going to see more attention given to the higher molecular weight products. Ethylene could be considered as a precursor for the production of synthetic fatty acids in the C-12 to C-14 range or, perhaps, for the acids in the C-20 to C-24 range. Economics will be most important.

I should have mentioned before that with the large variety of streams that the petrochemical manufacturer has available to him, he is not necessarily restricted to the production of either odd or even numbered carboxylic acids; he can take his pick, the limiting factors being the olefins selected and the technology used.

DR. RUTKOWSKI: Yes, that is right. One of the things that we have to consider when we talk about large volume economies is that there are certain limitations on batch operations, and, in order to take maximum advantage of our knowhow, we would almost need continuous processing. When we go to continuous processing, we do not always get only the one product we want, we might get a "smear" of things; therefore a situation might develop where the real problem would be marketing a group of products, one of which may be greatly desired, but others of which are not nearly so desirable. This could be the real major problem.

DR. SONNTAG: I think that each of you has made a number of very strong points. You said, in the first place, that ethylene, while not replenishable in the sense that a vegetable oil is, is nevertheless, cheap and abundant. And you have made the point that certainly, in the long run, the petrochemical industry can fractionally distill more cheaply (your columns are taller, that is certain!), and you also stated that you prefer continuous processing whenever and wherever possible, whereas the natural fatty acid industry largely employs batch operations. I expect that is true. On the other hand, I doubt that the fatty acid industry, exclusive of the tall oil part, makes 50 million pounds a year of any single fatty acid at any one location, so maybe continuous processing may be overemphasized as an advantage. You have a multitude of convincing factors, however. Your industry is big, it is efficient, and it is capable of making large amounts of products cheaply. You have already proved that with synthetic glycerine, long-chain alcohols, and polyethylene.

I should like to make a comment on this general situation here. The problem we are discussing is not unlike the advent of synthetic glycerine. This development caused quite some concern among the natural fatty acid industry about 10–15 years ago. We might draw a parallel between this threat and the synthetic glycerine situation. While, of course, the natural fatty acid industry has never been happy about it, the situation has settled down to a satisfactory status-quo. There are customers for natural glycerine as well as customers for synthetic glycerine. And the big worry on the part of the natural fat splitters has not materialized: expanding markets for glycerine have taken care of almost everyone's products.

We might also mention the threat of tall oil fatty acids which created another crisis as little as five to eight years ago. This development has now been stabilized within the overall fatty acid industry. Not only have tall oil fatty acids grown in volume themselves, but they have provided a number of new uses for some natural fatty acids available from fats and oils, and have also provided the fatty acid derivative manufacturer with a cheaper raw material out of which to produce certain profitable fatty acid derivatives. Things in technological progress are usually good for both sides. I think it is good to keep in mind that this situation is not new. We have gone through a history of new products coming in and perhaps partially replacing older products, and in so doing, stimulating and increasing their growth.

Gentlemen, we shall change the point of view and get down to specific products and talk about them in a little more detail. I should like to turn the microphone over for a little more extended time to Dr. Fefer, who will provide us with more details about Enjay's "Neo Acids."

Neo Acids Chemistry and Applications[1]

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Abstract

Four commercial neo acids (synthetic trialkylacetic acids) C_5, C_7, C_{10}, and C_{13} are synthesized employing an olefin, carbon monoxide, and acidic catalyst and possess the hindered neo configuration around the *alpha* carbon. Esterification using simple alcohols and polyols, and preparation of peroxyesters and metal salts using neo acids as well as toxicity, LD_{50} values of the acids, are discussed. Hydrolytic stability of the esters, and possible end use applications are described.

Introduction

THE NEO ACIDS are sterically hindered trialkylacetic acids available from the Enjay Chemical Company. They are prepared by reacting an olefin and carbon monoxide in the presence of an acid catalyst and water. The neo acid therefore contains one carbon more than the starting olefin. For example, to prepare trimethylacetic acid (pivalic acid or neo pentanoic acid), isobutylene and carbon monoxide are reacted in the presence of an acid catalyst yielding an isobutylene-carbon monoxide-catalyst complex. This complex is reacted with water to yield the crude carboxylic acid which is then purified. The mechanism for such a reaction using isobutylene as an example would be:

$$CH_2 = C(CH_3)_2 + H^{\oplus} \rightarrow (CH_3)_3C^{\oplus} \quad [1]$$

isobutylene catalyst carbonium ion

$$(CH_3)_3C^{\oplus} + C = O \rightarrow [(CH_3)_3C\text{–}CO]^{\oplus} \quad [2]$$

acyl carbonium ion

Hydrolysis then leads to the trialkylacetic acid and regenerates the catalyst:

$$[(CH_3)_3C\text{–}CO]^{\oplus} + HOH \rightarrow (CH_3)_3C\text{–}COOH + H^+ \quad [3]$$

neo pentanoic or pivalic acid

For the C_7, C_{10} and C_{13} neo acids, the starting olefins are C_6, C_9 and C_{12} respectively.

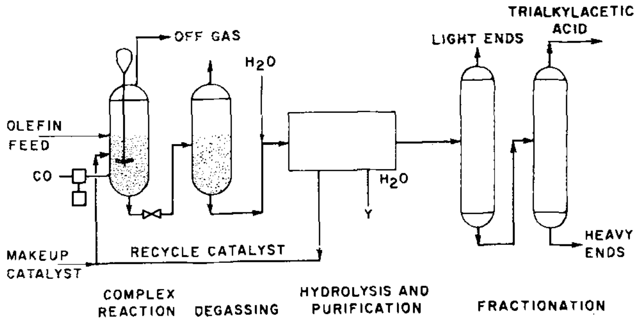

FIG. 1. Flowsheet for trialkylacetic acids process.

The flow diagram shown in Fig. 1 illustrates the basic process steps. Olefin feed and catalyst are pumped to reaction pressure and fed to the complexing reactor while a gas, rich in CO, is compressed and bubbled into the reaction mixture. After degassing, the complex proceeds to a hydrolysis tank where water is added to generate the neo acid and release the catalyst for reuse. The crude acid is then treated to remove the last traces of catalyst and is distilled to remove light and heavy ends.

The C_5 neo acid (trimethylacetic acid) has a purity greater than 99.5% as determined by gas chromatographic analysis and is an isomerically pure compound. Neo heptanoic acid (C_7) is about 95% 2,2-dimethylpentanoic acid with the remainder being 2-methyl-2-ethylbutanoic acid. This latter composition remains liquid below −40C. A typical analysis for alkyl groups on the *alpha* carbon for neo decanoic acid is shown in Table I. This analysis is also typical of the alkyl grouping of the C_{13} neo acid.

In general, reactions which use a mechanism that does not involve the carbonyl group (e.g., metal salt formation) proceed at rates comparable to "normal" fatty acids. If the carbonyl of the neo acid is involved (e.g., esterification) the rate will be slower than with a fatty acid. However, comparable rates can be achieved through using slightly more vigorous reaction conditions.

TABLE I
Neo Decanoic Acid, Analysis of Alpha Carbon Configuration

Alkyl groups	Percentage	Precision
2,2-Dimethyl	31	± 5
2-Methyl-2-higher-alkyl	67	±10
2,2-Di-higher-alkyl	2	±10

[1] Presented in part at AOCS Meeting, Los Angeles, April 1966.