

PALM OIL FATTY ACIDS IN SOAP AND DETERGENT FORMULATIONS

TABLE VI
Derivatives and Applications of Fatty Acids

Fatty acids	Derivatives	Applications
Palm fatty acid/pure palmitic/stearic acid	(1) α -Sulfo fatty acid (2) Alcohol sulfate (3) Ethylene oxide, propylene oxide condensate and epoxies (4) Alkanol amide sulfate (5) Amine derivatives, ethoxylated (6) Ethoxylated oleic acid dimer (7) Fatty alcohols: monoglycerides, ethoxylated and acetylate	(1) In detergent powder along with olefin sulfonated products (2) Biodegradable detergents (3) In nonionic detergent (4) In lime soap dispersing agents (5) Emulsifying agents in textile and other formulations (6) Nonionic detergent (7) Cosmetic formulation (15-30%)

soaps may be difficult to emboss without storage. When there is a stearic acid-rich oil in combination with palm acid oil, the hardness of the soaps is much increased, and as a result there is improved rate of extrusion in the Mazzoni equipment and also direct embossing. Similar results are obtained when an oil containing more stearic acid and arachidic acid is used along with palm acid oil.

This study, therefore, indicates that palm oil fatty acid in combination with higher saturated fatty acids can replace the tallow fatty acids in making soaps.

Table VI shows that palm oil fatty acid or pure palmitic acid, oleic acid and even stearic acid (made by hydrogenation) which can be isolated from palm oil fatty acids can be used in making a number of surface-active agents using known production technologies. These surface-active compounds find uses in different detergent formulations as

emulsifying agents in textile and other formulations. The fatty alcohols are used directly in cream formulations.

In India, tallow is difficult to obtain on a regular basis for use in soap production and, recently, its import has been very much restricted. On the other hand, palm oil fatty acids or palm acid oil and even high vacuum steam-stripped palm fatty acids from physical refining plants can be imported in view of lower cost and guaranteed availability for the purpose of producing soaps in combination with the minor oils in India and also for making surface-active compounds other than soaps.

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Hydroformylation of Unsaturated Fatty Acids

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ABSTRACT

When hydroformylation of unsaturated fatty materials is done with rhodium-triphenyl phosphine (or phosphite) catalysts, a number of advantages become apparent compared to cobalt carbonyl-catalyzed reactions. With rhodium, the reaction can be carried out (a) at pressures as low as 200 psi, (b) at each double bond location in a polyunsaturated fatty acid, and (c) in high yield and conversion. Solubilized catalyst can be recovered from distillation residue and reabsorbed on spent catalyst support by thermal treatment in a rotary kiln. The reconstituted catalyst is more active than the original catalyst and can be recycled indefinitely at a relatively low cost. Recently developed supports for "homogeneous" catalysis may make catalyst recovery even more effective. Acetalation, oxidation with air to polycarboxylic acids and catalytic hydrogenation to hydroxymethyl compounds can be done easily and in high yield on mono-, di- and triformal derivatives alike. Other reactions investigated for monoformal fatty esters include reductive amination to form aminomethyl derivatives and Tollen's condensation with formaldehyde to form geminal *bis*-hydroxymethyl compounds. Although the Northern Center has carried out some basic investigations on the hydroformylation reaction and on the chemistry of the hydroformylated products, there is a great deal more that can be done with regard to synthesis of new compounds and development of new applications.

INTRODUCTION

The reaction of synthesis gas with olefins in the presence of cobalt carbonyl as a catalyst, producing isomeric mixtures of aldehydes, was discovered by Otto Roelen in the laboratories of Ruhrchemie AG and first reported in 1938 (1-3). The reaction is identified variously as the Roelen reaction, the oxo synthesis or the hydroformylation reaction. Since its first application, it has rapidly become one of the most important industrial reactions, and 4-5 million metric tons of products are produced annually. The reaction is applied to propylene, e.g., in the synthesis of butyraldehyde, from which 2-ethyl-1-hexanol is made for producing di(2-ethylhexyl)phthalate, an important primary plasticizer for vinyl plastics. More recently, rhodium carbonyl catalysts have been applied to hydroformylation and other reactions with great commercial success in spite of the high costs of rhodium.

Both catalyst systems have been investigated for the hydroformylation of unsaturated fatty materials, but apparently this application is not now used on a large industrial scale. Failure to apply hydroformylation to unsaturated fatty materials probably can be ascribed to the wide dis-

crepancy in prices that used to exist between these materials and petrochemical olefins as feedstock. Although the hydroformylation of unsaturated fatty compounds has been reviewed previously (4-6), the present competitive pricing of unsaturated vegetable oils and animal fats compared to petroleum-derived olefins makes the following overall review pertinent.

COBALT CARBONYL CATALYST

Several years after the first Roelen disclosures (1,7), patents on the hydroformylation of unsaturated fatty acids were issued to several different companies, including du Pont (8), General Mills (9), B. F. Goodrich (10,11), Henkel (12), Rohm and Haas (13-16), Ruhrchemie (17) and Standard Oil (18,19). In general, reaction conditions for conventional hydroformylation included pressures of 2000-5000 psig of synthesis gas, temperatures of 100-200 C, in either the presence or absence of a solvent (benzene, toluene), and with the cobalt catalyst formed in situ from several different cobalt compounds (Fig. 1). Natta and Beati (20) describe hydroformylation of methyl oleate, olive oil and grapestone oil at 110-150 C and at ca. 300 psig with a basic cobalt carbonate catalyst containing 2% basic iron carbonate on a bentonite support. Cobalt (II) acetate at a concentration of 0.5% favors aldehyde ester formation; at a concentration of 2%, the reaction proceeds more quickly and favors hydroxymethyl ester formation (21). With methanol as a solvent, the acetals of methyl formylstearate are formed (13).

With cobalt acetate as the catalyst and a 2:1 ratio of CO/H₂, the hydroformylated product is favored at 150 C and high pressures; but at 190 C with a CO/H₂ ratio of 1:2 and low pressures, the hydroxymethyl derivative is favored (22). The hydroxymethyl compounds form polyesters and estolides, but these can be saponified easily to the original compound (4).

Oleyl alcohol and oleyl nitrile, but not oleyl amine, can be hydroformylated as easily as methyl oleate (23).

With dicobalt octacarbonyl as catalyst and at a temperature of 100-110 C and a pressure of 3500-4500 psig, 85% yields of distillable methyl formylstearate have been reported (24). With polyunsaturated esters, mainly the monoformyl derivative is obtained, because isomerization, conjugation and hydrogenation occur so much more rapidly than hydroformylation. Hydroformylation at 175-200 C produced the hydroxymethyl derivatives.

Double bond isomerization, both geometric and positional, occurs to a considerable extent with cobalt catalysts before hydroformylation takes place. The product is a mixture of isomers with the preponderance of reaction at the 9,10-position of methyl oleate, but with as much as 6-10% of the linear product having been formed as the result of addition to double bonds in the terminal position (25). Positional isomerization does not occur at 150 C, but extensive isomerization occurs at 190 C. Others have also shown the formation of linear formylated products (17,24).

Frankel (26) showed that the hydroformylated reaction product could easily be converted to more stable intermediates and recovered by distillation as the acetal or as the acetylated hydroxymethyl derivatives. For example, hydroformylation of methyl oleate at 120 C, followed by treatment with methanol to make the acetal and then with aqueous sodium carbonate to destroy cobalt carbonyl, and finally distillation, produced methyl 9(10)-dimethoxymethylstearate in 95% yield. If distillation was done without first destroying the catalyst, the product was methyl 9(10)methoxymethylenestearate.

When hydroformylation was done at 120 C and the

temperature then raised to 180 C, the hydroxymethyl derivative was formed and metallic cobalt was precipitated. Recovery of the catalyst by filtration and recycling were then possible. The reaction product could be distilled in 95% yield when first saponified and then acetylated.

RHODIUM CATALYSIS

In 1970, Frankel of the Northern Regional Research Center announced the application of a highly selective rhodium catalyst system for the hydroformylation of methyl oleate, the details of which were published in 1971 (27) and 1974 (28) (Fig. 2).

The following conditions applied with a 1:1 mixture of carbon monoxide and hydrogen (synthesis gas): catalyst, rhodium (5%); support, CaCO₃, C, Al₂O₃; catalyst amount, 0.05-0.2 g Rh/100 g oleate; ligand, triphenyl phosphine; ligand, 0.5-4.0 g/100 g oleate; pressure, 1000-2000 psig; temperature, 100-110 C; time 4-6 hr.

A solvent, such as toluene, could be used but was not necessary. Typically, a solvent concentration of 60 mL/100 g of oleate was used. Conversion of methyl oleate to distillable methyl formylstearate under these conditions was from 90 to 99%. Thin layer chromatography and mass spectroscopy were used to demonstrate the product (as the carbomethoxystearate derivative) to be an equimolar mixture of methyl 9-formylstearate and methyl 10-formylstearate, hereinafter referred to as methyl 9(10)-formylstearate.

The effective catalyst was shown to be a solubilized rhodium compound, complexed with triphenyl phosphine, which was concentrated in the residues after distillation of the formylstearate.

In later studies at the Northern Center, Friedrich et al. (29,30) demonstrated a method in which the solubilized catalyst from distillation residues was recovered and re-deposited (Fig. 3). The catalyst was active and could be re-

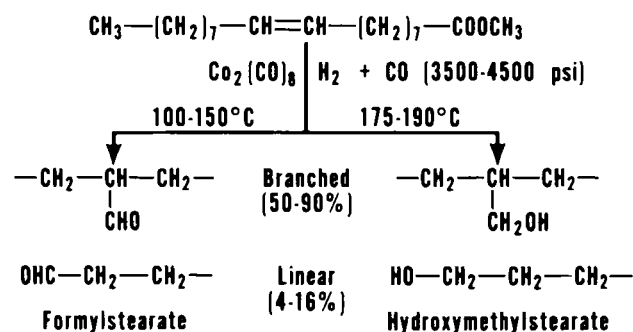


FIG. 1. Conventional hydroformylation with cobalt carbonyl.

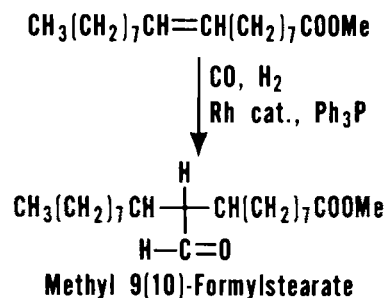


FIG. 2. Selective hydroformylation of methyl oleate with rhodium-triphenyl phosphine catalyst.

HYDROFORMYLATION OF UNSATURATED FATTY ACIDS

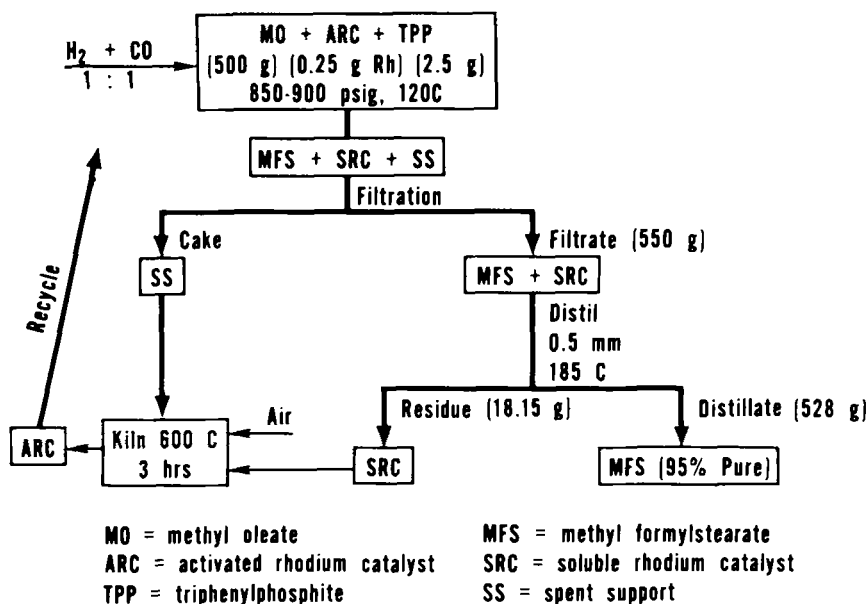


FIG. 3. Process flow diagram for the recovery and resupport of rhodium catalysts.

cycled at least 10 times with no significant loss in activity.

For purposes of cost effectiveness in the recovery process, the support was changed to Al_2O_3 in place of CaCO_3 , and the ligand used was triphenyl phosphite in place of the phosphine. Distillation residue, containing the solubilized catalyst, together with the spent catalyst recovered by filtration from the reaction product, were heated in a gas-fired rotary kiln to temperatures of ca. 300 C and subsequently to ca. 600 C to destroy organic matter, which includes the triphenyl phosphite. Recovery of activated rhodium catalyst amounted to at least 80% after 10 cycles, or an average loss of less than 2% for each individual run.

Based on a catalyst make-up of 2%, a processing cost of 13.7 ¢/lb of product was calculated (29). One-fourth of the processing cost, which did not include cost of starting material, resulted from the 2% catalyst make-up.

Use of rhodium catalyst that had been recovered and activated as described above permitted considerable reduction in the pressures necessary for hydroformylation. The conditions that applied included the following (31): catalyst, activated rhodium (5%); support, Al_2O_3 ; catalyst amount, 0.05 g Rh/100 g oleate; ligand, triphenyl phosphite; ligand, 1.0 g/100 g oleate; pressure, 200 psig; temperature, 110-150 C; time, 2-7 hr; solvent, none.

The shorter times, of course, apply to the higher reaction temperatures. The higher temperatures resulted in irreversible decomposition of the catalyst complex and formation of two unidentified byproducts. Essentially quantitative conversion of methyl oleate to methyl 9(10)-formylstearate was achieved in 4 hr at 120 C.

The lower pressures make feasible the use of standard hydrogen equipment for hydroformylation, permitting lower costs for the equipment than when higher pressures are required. Cost calculations have not been made for the reaction involving low-pressure equipment.

The reactivated rhodium catalyst is probably not more active as such, but it is probably more soluble in the substrate compared to the initial rhodium product.

Rhodium can also be recovered from crude methyl formylstearate in more than 98% yield by extraction with an aqueous mixture of hydrogen cyanide and triethanol-

amine (TEA) (32). Recovery was only 90% when tried with crude hydroformylated methyl esters from soybean oil with the same proportion of reagents (0.5% hydrogen cyanide, 0.5% TEA and 5% water). Recovery was again more than 98% with both hydroformylated soybean and safflower methyl esters when the amount of reagents was doubled.

Other methods for recovery of rhodium have been reported (33,34).

HYDROFORMYLATION OF OLEIC ACID

Oleic acid as well as oleate esters can be used as a starting material for the hydroformylation reaction with either cobalt carbonyl (26) or rhodium catalysts (35). With the cobalt catalyst, a 96% yield of methyl 9(10)-dimethoxymethylstearate and a 90% yield of methyl 9(10)-acetoxy-methylstearate were recovered by distillation.

With the rhodium catalyst, a one-step esterification-acetalation process was developed in which methanol, from which water was removed by use of molecular sieves, was continuously recycled (35) (Fig. 4). The double reaction was catalyzed by an ion-exchange resin in the acid form to

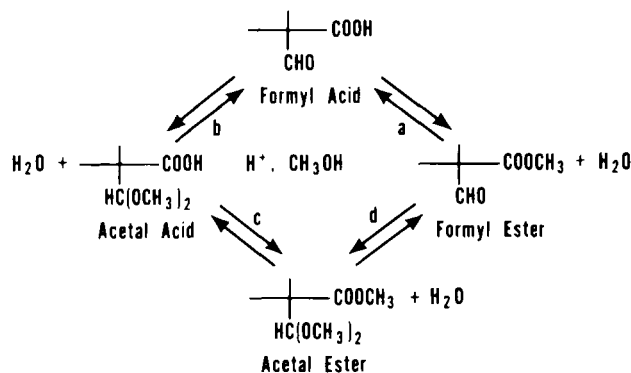


FIG. 4. Simultaneous esterification-acetalation of hydroformylated oleic acid.

avoid build-up of inorganic salts in rhodium. The rhodium was recovered and activated from distillation residues as before. The crude acetal ester (still containing the rhodium) was then distilled to form methyl 9(10)-methoxymethylenestearate in ca. 90% yield (Fig. 5). Rhodium could be recovered and resupported if triphenyl phosphine but not the phosphite was used as the ligand.

HYDROFORMYLATION OF POLYUNSATURATED FATTY COMPOUNDS

In contrast to the results obtained with cobalt carbonyl in the hydroformylation of polyunsaturated fats, each of the double bonds in a fatty acid chain can be hydroformylated in good yield with rhodium (28,36,37). Thus, hydroformylation of methyl linoleate and linolenate with rhodium-triphenylphosphine yields 1,4-diformyl esters as major and 1,3-diformyl esters as minor products (Fig. 6). Triformyl esters are produced from linolenate. Unsaturated and saturated monoformyl esters can also be produced, depending on whether or not the reaction is carried to completion.

Highest yields of diformyl products (75% from safflower methyl esters) were obtained if hydroformylation was first carried out at 90 C, then at 110 C, until gas absorption ceased at each step (38).

REACTIONS OF HYDROFORMYLATED PRODUCTS

The aldehyde group is well known as a versatile functional group able to undergo a wide variety of reactions, including acetalation, oxidation, reduction, reductive amination and the Tollen's condensation.

Acetalation

Formation of dimethyl acetals and their cleavage to enol ethers have already been mentioned. Acetalation is easily accomplished with aliphatic alcohols in the presence of an acidic catalyst, provided that the water produced in the reaction can be removed. Acetals made with lower aliphatic alcohols readily undergo exchange reactions, and the exchange can be made quantitatively when the lower alcohol is removed from the reaction site by distillation. Thus, cyclic acetals are easily made from glycerol (39), glycols and spiroacetals from pentaerythritol (40) (Fig. 7). The pentaerythritol acetal of methyl formylstearate is an interesting bifunctional compound capable of undergoing polycondensation reactions. It can be formed directly from the formylstearate or from the dimethyl acetal or the enol ether, methyl 9(10)-methoxymethylenestearate.

An interesting reaction is the selective alcoholysis of acetal esters in the presence of basic catalysts (40). Thus, various esters can be prepared by transesterification with no effect on the acetal group. Similarly, transacetalation can be carried out in the presence of acidic catalysts (Fig. 8).

Aminolysis

Hydroxymethyl derivatives (obtained by hydroformylation followed by reduction of the hydroformylated derivatives of methyl oleate, linseed oil and safflower oil) undergo aminolysis very readily with diethanolamine in the presence of sodium methoxide catalyst (41).

Oxidation

The formyl group reacts rapidly with atmospheric oxygen to form a carboxyl group under appropriate catalytic conditions, thus forming a 19-carbon dibasic acid. Sparging a 25% solution of methyl 9(10)-formylstearate with air at 20 C resulted in 80% conversion in 1 hr when 0.05% manganese naphthenate was the catalyst (42-44). More than

10% byproduct keto- and hydroxystearic acids were formed. The byproduct formation was minimized (to 0.8%) when calcium naphthenate (0.5%) was also present, but the reaction was less rapid. Conversion was 95% in 7 hr with the binary catalyst. Permanganate oxidation is also effective (27,45).

A more convenient procedure involves taking advantage of the presence of soluble rhodium catalyst in crude methyl formylstearate to catalyze oxidation as well as hydroformylation (46) (Fig. 9). The oxidation is carried out at 25 C in the same autoclave used for hydroformylation with

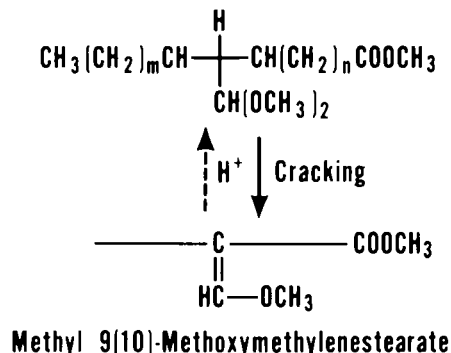


FIG. 5. Formation of methyl 9(10)-methoxymethylenestearate.

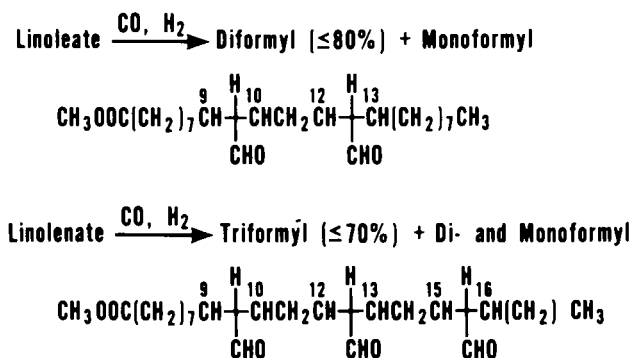


FIG. 6. Hydroformylation of polyunsaturated fatty esters to produce di- and triformyl derivatives.

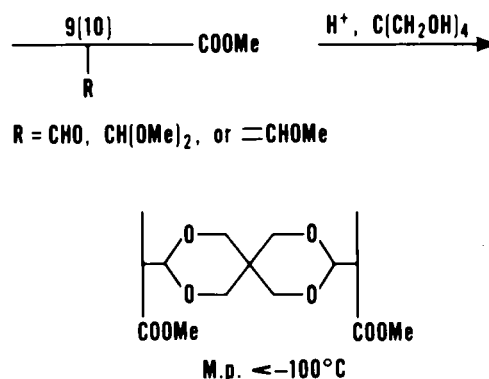


FIG. 7. The pentaerythritol acetal of methyl 9(10)-formylstearate.

HYDROFORMYLATION OF UNSATURATED FATTY ACIDS

either oxygen or air and with the crude reaction product emulsified with water (40%). Conversion is 87-89% in 2-3 hr, 93-95% when calcium acetate (2%) is added. Methyl formylxystearate was identified as a byproduct in addition to methyl keto- and hydroxystearate. The presence of calcium compounds in regenerated rhodium catalyst does not have a deleterious effect on rhodium activity for hydroformylation, provided acetic acid is added to regenerate calcium acetate.

The two carboxyl groups in 9(10)-carboxystearic acid have different activities with regard to esterification and transesterification. The terminal carboxyl group is 26-27 times more reactive in esterification and twice as reactive in transesterification compared to the internal carboxyl group (45). It thus becomes possible to make mixed esters such as 2-ethylhexyl 9(10)-carboxymethoxystearate (47).

In mixtures of methyl mono-, di- and tricarboxystearates, obtained from soybean methyl esters, e.g., the strongly acidic polycarboxylic esters can be separated from the less acidic monocarboxylic ester by serial extraction with dilute sodium hydroxide or sodium bicarbonate solutions (47,48).

Reduction

Hydrogenation of the formyl group to the hydroxymethyl group has already been described. Hydroformylation with cobalt carbonyl at 120 C followed by hydrogenation at 180 C is the two-step process involved.

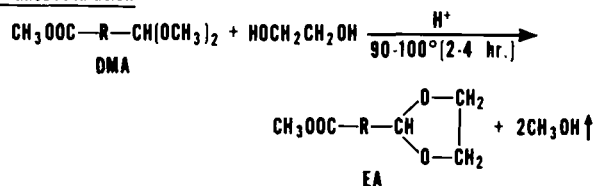
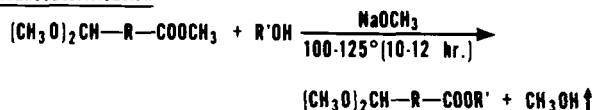
Transacetalation**Transesterification**

FIG. 8. Selective transacetalization and transesterification of methyl 9(10)-dimethoxymethylstearate.

Hydrogenation also takes place readily with Raney nickel at ca. 100 C and 500-1000 psig of hydrogen (27). Methyl hydroxymethylstearate may also be prepared by sodium borohydride reduction (27).

Reductive Amination

Reaction of methyl formylstearate with aqueous ammonia in methanol over Raney nickel at 100 C for 2 hr produced a 53% yield of 9(10)-aminomethylstearic acid (Fig. 10) (49). Polymers made from this amino compound were generally of lower molecular weight and lower softening point compared to those made from the isomeric carboxyoctadecylamine.

Polycondensation Reactions

Poly(ester-acetals) and poly(amide-acetals) prepared from the pentaerythritol acetal of methyl formylstearate have latent crosslinking functionality that can be activated in the presence of heat and an acidic catalyst (Fig. 11) (50). Similarly, poly(ester-acetals) can be made by the self-condensation of the glycerol acetal of methyl formylstearate.

Polyamides, copolyamides and reactive polyamides from the 19-carbon 9(10)-carboxystearic acid have been prepared and characterized (51). Physical properties of 9(10)-carboxystearic acid are such that it is possible to separate the isomers by recrystallization from *n*-heptane (52). 9-Car-

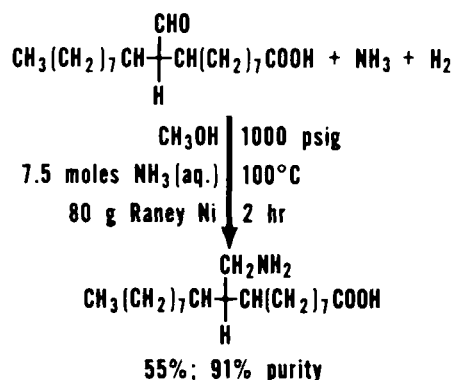


FIG. 10. Reductive amination of 9(10)-formylstearic acid.

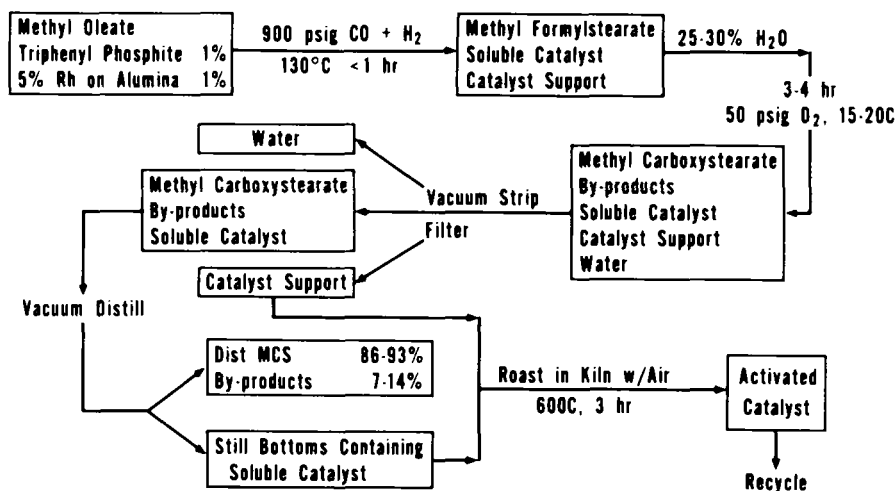


FIG. 9. Process flow diagram for making methyl carboxystearate by air oxidation.

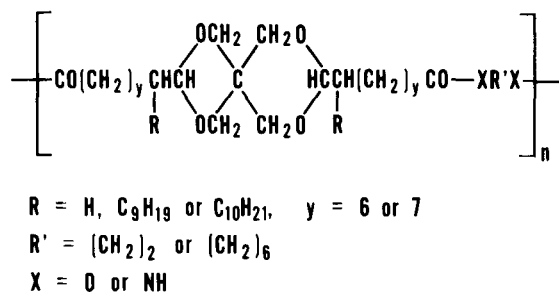


FIG. 11. Poly(ester-acetals) and poly(amide-acetals) from the pentaerythritol acetal of methyl 9(10)-formylstearic acid.

boxystearic acid is an alkyl-substituted derivative of sebacic acid and has a higher melting point than 10-carboxystearic acid, as expected. The alternating effect in even- vs odd-numbered straight-chain dicarboxylic acids is well known. Apparently, the effect carries over to the substituted derivatives as well.

Tollen's Condensation

This reaction involves the condensation of formaldehyde with an aliphatic aldehyde having an α -hydrogen, followed by a crossed Cannizzaro reaction to produce geminal bis-hydroxymethyl derivatives. It is a commercially used reaction to produce polyols such as pentaerythritol and trimethylolpropane.

When applied to 9(10)-formylstearic acid, the reaction proceeds quantitatively, and the product is 9,9(10,10)-bis-hydroxymethylstearic acid (Fig. 12) (53). Applications for these and similar long-chain polyols have been explored (54-58).

APPLICATIONS FOR FATTY OXO DERIVATIVES

Potential applications for the various oxo derivatives are numerous and have been reviewed (6). Only a listing is given here to illustrate some of the possibilities (Fig. 13): coatings (59,60); lubricants (47); plasticizers (38-40,54-56, 61-64); polyamides (40,51,52,65-69); poly (amide-acetals) and poly (ester-acetals) (50,70); urethane foams (41,71-73); and wool shrink-resist treatment (74).

RESEARCH FOR THE FUTURE

Although several aspects of hydroformylation chemistry have been investigated, the research reported herein is only a small part of the research that could be carried out. Among the many research areas that are of interest both academically and industrially are:

- improved recovery of catalyst, perhaps by means of a heterogenized catalyst system.
- chemistry of polyformyl fatty compounds,
- chemistry of unsaturated formylated compounds.

The Northern Center has terminated its research, and has no plans for the future, in this area. It is to be hoped that others will see fit to continue this research as a means of solving socioeconomic needs with renewable resources.

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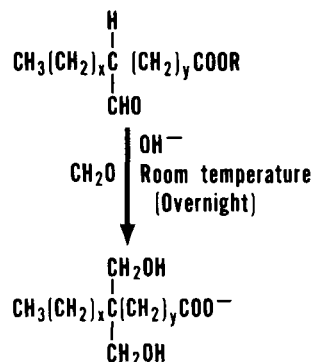


FIG. 12. Formaldehyde condensation reaction with methyl 9(10)-formylstearate to make 9,9(10,10)-bis-hydroxymethylstearic acid.

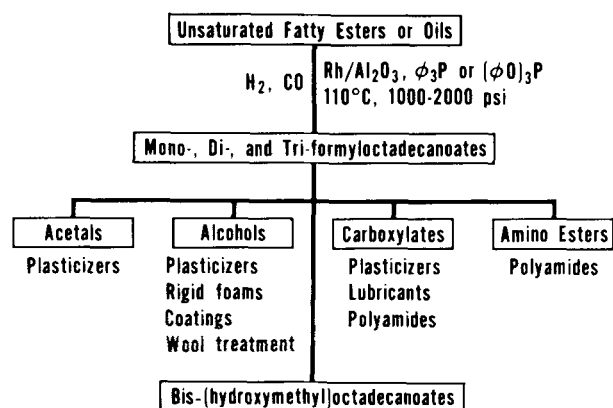


FIG. 13. Hydroformylated unsaturated fatty compounds, their derivatives and their potential application.

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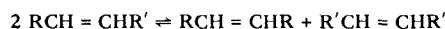
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Metathesis of Fatty Acid Esters

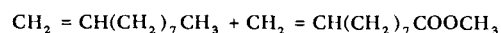
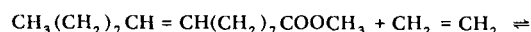
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ABSTRACT

In metathesis reactions, unsaturated compounds are converted into new compounds via an exchange of alkylidene groups:



Since its discovery in 1964, this catalytic reaction has found several large-scale applications in petrochemistry. One of the most promising synthetic applications of metathesis is to functionalized olefins such as unsaturated esters, ethers, amines, etc., because this allows single-step syntheses of a variety of mono- and difunctional hydrocarbon derivatives. Unfortunately, however, most metathesis catalysts are easily poisoned by polar groups. In 1972 in our institute, the $\text{WCl}_6\text{-(CH}_3)_4\text{Sn}$ system was found to be effective as a catalyst for homogeneous metathesis of fatty acid esters. Thus methyl oleate was converted into 9-octadecene and dimethyl 9-octadecene dioate, starting materials for the synthesis of valuable chemical products. In 1977 we developed a heterogeneous catalyst system: Re_2O_7 on Al_2O_3 , activated with a small amount of $(\text{CH}_3)_4\text{Sn}$. Systematic research has led to interesting applications of metathesis and cometathesis reactions with these catalysts. An example is the cometathesis of methyl oleate with ethene, to produce shorter-chain compounds with terminal double bonds:



Cometathesis of olive oil (mainly triolein) with ethene opens the possibility of producing both α -olefins in the C_{10} range and fatty oils with lower molecular weight (palm oil type). Until now, metathesis of fatty esters has been restricted mainly to synthetic purposes. Large-scale applications depend mainly on the development of more active and cheaper catalyst systems.

INTRODUCTION

The catalytic metathesis of olefins, a reaction discovered by Banks and Bailey in 1964 (1), can be described as an exchange of alkylidene groups in the participating molecules to form new unsaturated molecules:

