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FATS - VERSATILE RAW MATERIALS FOR CHEMICAL USE

By

Daniel Swern

ABSTRACT

(For List of Publications)

Several important chemical reactions of fats and fatty acids are briefly reviewed. These include epoxidation, monohydroxylation, dihydroxylation, maleic anhydride addition and the preparation of nitrogen derivatives, dimer acids and vinyl esters.

FATS - VERSATILE RAW MATERIALS FOR CHEMICAL USE

By

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Fats have been known to man since prehistoric times but how or why man chose to use fats for food and non-food uses is unknown. Although fats have been known for a long time, the bulk of our present day uses differ only slightly from the original ones. At the risk of getting ahead of myself it should be pointed out that with the exception of glycerol, fats have generally not been used as sources of pure organic chemicals where the distinctive properties of substances are the basis for their industrial utilization. In two fields in which fats have always found a substantial outlet serious inroads have been made by other materials. The production of synthetic detergents, which are primarily non-fat based, has grown rapidly, mainly at the expense of soap expansion, and synthetic surface coating materials, such as rubber-based paints and vinyls, are taking the place of traditional drying oil products.

The failure of fats to change their role over the past few thousand years can be attributed in large part to their neglect by research workers. As a valuable recurring natural resource fats should have been the subject of intense investigation as sources of industrial chemicals. In the past twenty-five years progress in the chemistry of and the development of

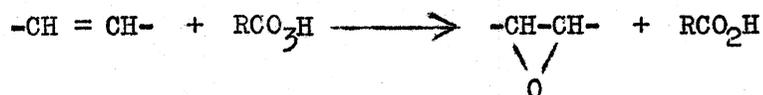
A Laboratory of the Eastern Utilization Research and Development Division,
Agricultural Research Service, U. S. Department of Agriculture.

industrial chemicals from fats has indeed been gratifying. The main reason for this is an awareness on the part of the scientist and business man of the value of fats. Other reasons are ready availability, low price, and the by-product nature of some fats. We have already accumulated a sufficient body of fundamental data regarding the reactivity of fats and their component acids that the ingenious scientist can write numerous chemical reactions which have a reasonable chance of being successful not only in the laboratory but also on a large scale. The field is far from exhausted, however, and there are still numerous important areas in fat chemistry which require a large amount of fundamental investigation.

It seems reasonable to assume, then, that even though progress in the industrial utilization of fats is a much belated phenomenon it is inevitable that fats will also become the source of large quantities of pure chemicals. In the not too distant future there will undoubtedly be a large family of "oleochemicals" from fats comparable to "petrochemicals" from petroleum.

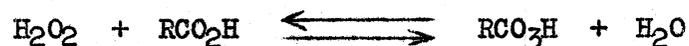
The remainder of this article will be devoted to chemical reactions which are (a) already being employed on an industrial scale, (b) show promise of industrial acceptance or (c) illustrate the versatility of fats in the synthesis of interesting types of organic compounds. Since fats are made up mainly of fatty acid esters, most of the reactions to be discussed are reactions of the fatty acid moiety.

EPOXIDATION: Epoxidation is the conversion of an olefinic double bond to the oxirane group by reaction with an organic peracid, as illustrated by the equation:



The reaction was discovered in 1909 by the Russian chemist Prileschajew¹ who showed that perbenzoic acid is an efficient epoxidizing agent for isolated double bonds. It is an excellent reaction for laboratory use because it is often rapid under mild conditions in nonreactive organic solvents, and yields are high. Since the original discovery, over 350 olefinic compounds have been epoxidized and numerous other peracids have been shown to be usable, notably peracetic, monopero-phthalic and performic acid.²

The epoxidation reaction assumed practical importance only within the past ten years with the development of in situ techniques for preparing and using up performic³ and peracetic⁴ acids as they are formed. Since the preparation of peracids is an equilibrium, it is possible to avoid their separate preparation by conducting the reaction of hydrogen peroxide with the aliphatic acid in the presence of the olefinic compound to be epoxidized.



By operating in this way losses of active oxygen are kept at a minimum and the hydrogen peroxide can be efficiently utilized. The only epoxidation techniques which have achieved commercial importance are the in situ ones, using hydrogen peroxide with either formic or acetic acid as the oxygen carriers.

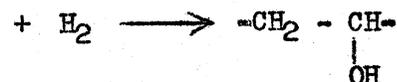
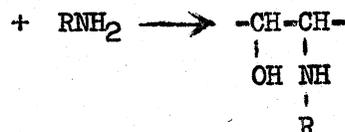
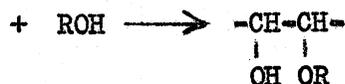
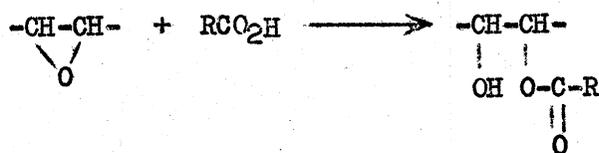
The introduction of the oxirane group into the alkyl chain of a fatty-acid ester markedly increases its compatibility with polyvinyl chloride and other resinous materials. Furthermore, the oxirane group reacts rapidly and quantitatively with hydrogen chloride thereby exerting a stabilizing effect on chlorine-containing polymers. These desirable characteristics

have resulted in the commercial use of epoxidized fatty-acid esters as stabilizing plasticizers for chlorine-containing polymers and copolymers, particularly polyvinyl chloride.⁵

Epoxidized soybean oil was the first commercially available epoxy fatty ester primarily because of its availability and relatively low price. Its limited compatibility with polyvinyl chloride, however, prompted research on the preparation of epoxy fatty esters which can be used as primary plasticizers.

Numerous simpler epoxy esters have since been reported. Thus, butyl, hexyl, and other alkyl epoxystearates have excellent compatibility with polyvinyl chloride and they impart outstanding low-temperature characteristics to the polymer. Alkyl epoxystearates are now commercially available, as are salts of epoxystearic acid.

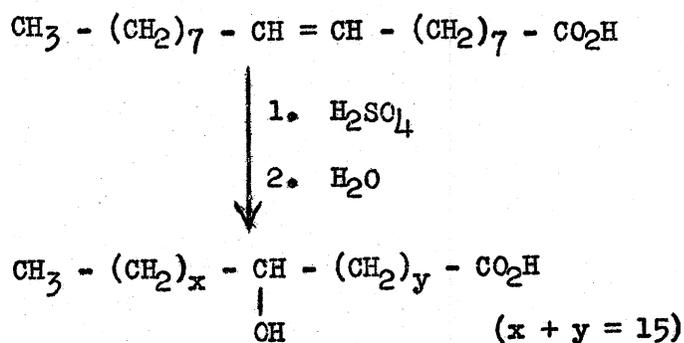
The oxirane ring in fatty acids is extremely reactive and, in addition to its reaction with hydrogen chloride already mentioned, it undergoes the following reactions with compounds containing active hydrogen atoms:



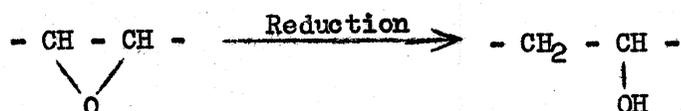
These products may be useful in the preparation of plasticizers, lubricants, or lubricant additives. Furthermore, epoxidized oils and esters can be employed in polycondensation reactions to prepare valuable surface coating materials.

MONOHYDROXYLATION: 12-Hydroxystearic acid, derived from castor oil by hydrogenation and hydrolysis, is an important component (as the lithium salt) of all-purpose greases for aircraft and other military uses. Furthermore, esterification of the carboxyl and hydroxyl groups with the appropriate alcohol and acid yields useful secondary plasticizers. Since castor oil is a nondomestic oil, recent research has been directed toward the preparation of monohydroxystearic acid from plentiful domestic sources, particularly oleic acid obtained from animal fats.

A mixture of isomeric monohydroxystearic acids is obtained in good yield from oleic acid by low-temperature addition of concentrated sulfuric acid followed by hydrolysis of the intermediate sulfate esters;⁶



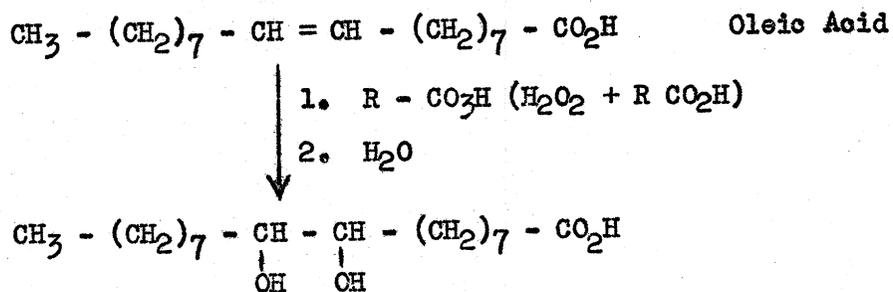
A convenient procedure for preparing monohydroxystearic acids of known structure is hydrogenation or chemical reduction of the corresponding oxirane;⁷



A recently discovered reaction for the synthesis of monohydroxy acids, and one which may have wide applicability both on a laboratory and on a commercial scale, is the addition of 90-100% formic acid at its boiling point to olefinic acids, followed by hydrolysis of the intermediate formate esters.⁸ The reaction rate is increased considerably by acidic catalysts, particularly perchloric and sulfuric acids and boron fluoride. The yield of monohydroxystearic acids from oleic acid is over 70%, with the 9- and 10- isomers predominating by far.

Numerous esters of monohydroxy fatty acids have been prepared. These have been suggested as high-melting waxes and release agents for plastics, and as intermediates in the preparation of plasticizers and surface-active agents. An interesting new potential use for diesters of monohydroxystearic acid is in the synthetic lubricant field.⁹

DIHYDROXYLATION: Two general and widely used methods are available for preparing contiguously substituted (α -glycol) dihydroxy fatty acids. These are epoxidation of the corresponding olefinic acid with organic peracids followed by hydrolysis² and oxidation of the olefinic acid with dilute, cold alkaline potassium permanganate.¹⁰ Yields of dihydroxy acids are good, often exceeding 90%. The peracid hydroxylation follows:

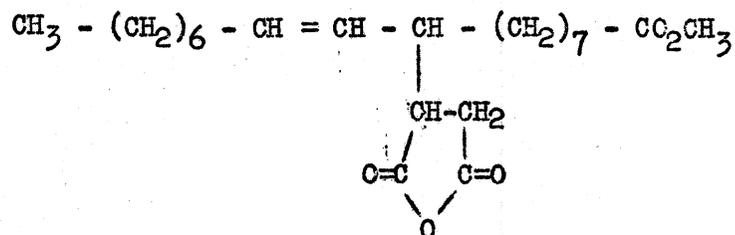


9,10-Dihydroxystearic acid

In peracid hydroxylations it is customary to use an in situ method with conditions arranged to cause opening of the oxirane ring as it is formed. The resulting hydroxy-acyloxy compound is more easily converted to the α -glycol than is the oxirane, and yields are essentially quantitative.

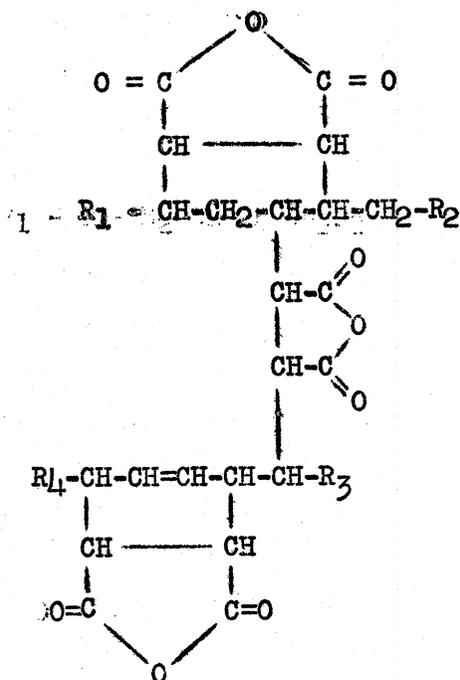
MALEIC ANHYDRIDE ADDITION: Drying oils modified by reaction with maleic anhydride have improved drying properties and are extensively used. The chemistry involved in such a complicated system is not known in detail but some recent work has been published on the reaction of maleic anhydride with pure unsaturated fatty esters, both conjugated and nonconjugated.

At 200° methyl oleate and maleic anhydride form at least four isomers.¹¹ The maleic anhydride attacks at the reactive allylic system, with corresponding double bond shift, yielding products substituted in the 8, 9, 10, or 11 position. The structures of these products are similar to that shown below.



Methyl linoleate and maleic anhydride give more complex products.¹² A small amount of a 1:1 adduct is formed which appears to be a Diels-Alder addition product of one mole of maleic anhydride with one mole of conjugated methyl octadecadienoate formed by isomerization under the conditions of the reaction. The predominant adduct, however, is polymeric and contains a multiple number of maleic anhydride and methyl linoleate units. One product which has been isolated appears to contain three maleic

anhydride and two methyl linoleate units. A possible structure, showing only the central portion of the linoleate molecules, is given below. Thus, maleic anhydride can react to connect two glyceride molecules containing linoleic radicals thereby acting as a bodying or thickening agent.

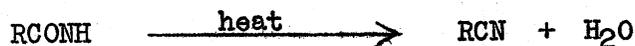


Maleic anhydride reacts with conjugated fatty acids by a Diels-Alder reaction. The reaction, under mild conditions, has been used to measure conjugation but is not nearly so good for this purpose as spectrophotometric analysis. The maleic anhydride adducts of α - and β -eleostearic acids have recently been used, together with physical and other chemical evidence, to demonstrate unequivocally that the structure of α -eleostearic acid is 9-cis, 11-trans, 13-trans-octadecatrienoic acid, and β -eleostearic acid is 9-trans, 11-trans, 13-trans-octadecatrienoic acid.¹³

Maleic anhydride adducts of unsaturated fatty acids contain three or

more carboxyl groups (or their equivalent in anhydride groups). These can undergo typical reactions of the carboxyl group to yield esters and amides, for example, or they can be used in polycondensation reactions. Maleic anhydride adducts of polyunsaturated fatty acids still contain double bonds which can be epoxidized and hydroxylated, to name only two potentially useful reactions.

NITROGEN DERIVATIVES: The most widely used long-chain nitrogen derivatives are amides, nitriles, amines and their reaction products, many of which are commercially available. They are usually derived from purified fatty acids by the following reactions:



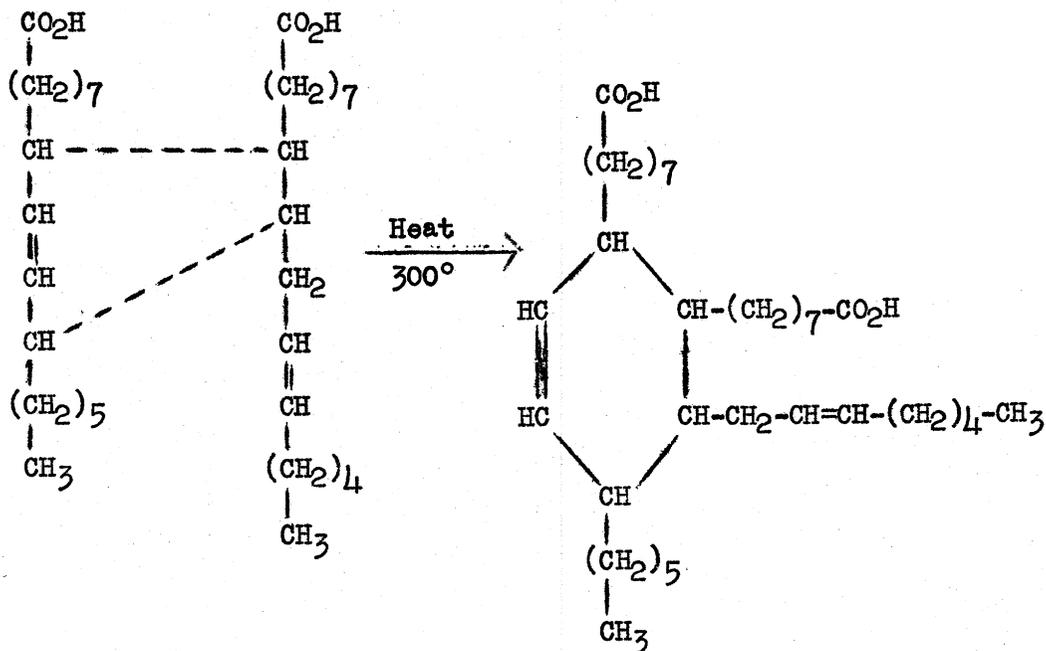
Amides can also be prepared in high yield by reaction of the glycerides with ammonia or amines. Amides are neutral substances and range in physical appearance from waxy solids (saturated) to pasty masses (unsaturated). Fatty acid amides are used as anti-block agents in plastic and wax formulations to reduce surface tack, as mutual solvents to increase the compatibility of synthetic resins with waxes, in printing inks as anti-offset and anti-scratch agents, as thickeners and stabilizers for emulsions, as dye solubilizers, and as "builders" in synthetic detergent formulations to enhance the detergent properties and increase foam stability. Fatty acid amides are also used for the synthesis of permanent textile water repellents and also in the preparation of a whole host of non-ionic surface active agents by condensation with varying amounts of ethylene oxide.

Fatty nitriles are useful as low temperature plasticizers for polyacrylonitrile and vinyl polymers, as yarn lubricants, in the synthesis of textile water repellents and, in one case (lauronitrile), as an insect repellent.

Fatty amines are basic and very reactive. They are insoluble in water but they can be readily converted to a water-soluble or water-dispersible form by reaction with acids to form ammonium salts. Fatty amines also react with acid chlorides or anhydrides to form N-substituted amides and they are readily converted to surface active and germicidal quaternary ammonium salts. In general, fatty amines show the same reactivity as the short chain primary and secondary amines.

Fatty amines are used in the rubber industry as reclaiming, mold release and accelerating agents; as retarders and anti-scorching agents for butyl rubber; in the textile industry for preparing cationic softening agents, dyeing assistants and anti-static agents; in froth flotation and agglomeration types of mineral concentration; as corrosion inhibitors; in the preparation of cationic surface active agents which are good emulsifiers and also have germicidal and algacidal properties; and in the preparation of non-ionic surface active agents by reaction with ethylene oxide.

DIMER ACID FORMATION. A comparatively new use for fats is the preparation of dimer acids from linoleic acid (9,12-octadecadienoic acid). When linoleic acid, its methyl ester or oils rich in linoleic acid are heated to about 300°, the linoleic acid chains dimerize.¹⁴ In this reaction, one molecule of linoleic acid isomerizes to a conjugated octadecadienoic acid, either 9,11- or 10,12-, and this in turn reacts with one molecule of unchanged linoleic acid by a Diels-Alder reaction, as shown:



9,11-Linoleic Acid

9,12-Linoleic Acid

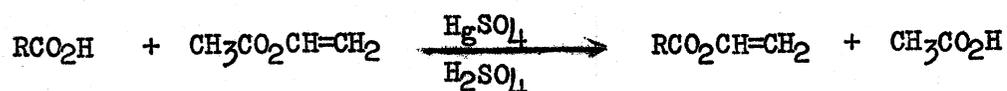
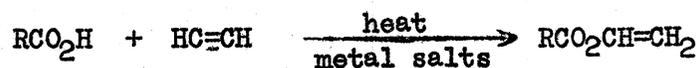
Dimerized Linoleic Acid

It is evident that a variety of geometric and position isomers can be formed by this reaction, and undoubtedly are.

Dimerized linoleic acid is a dibasic acid and undergoes the expected polycondensation reactions with glycols and diamines. The polyesters obtained with glycols are readily increased in molecular weight by reaction with diisocyanates; the resulting products can then be converted to foamed rubber articles. Polyamides are used as water-resistant adhesives, shellac substitutes, and nonblocking paper coatings. Coreaction of the polyamides with epoxy resins forms new high polymers with a wide range of flexibility depending on the components.

LONG CHAIN VINYL ESTERS. A potentially large chemical use for fats is the preparation of vinyl esters of long chain fatty acids for use in the preparation of polymers or copolymers with commercially important

monomers, such as vinyl acetate or vinyl chloride. The following equations show the preparation of vinyl esters by the reaction of fatty acids with acetylene under pressure or by an interchange reaction from fatty acids and vinyl acetate at atmospheric pressure:¹⁵



Long-chain vinyl ethers are prepared from the corresponding fatty alcohol.

The main interest in vinyl esters of long-chain fatty acids is in the preparation of internally plasticized copolymers in which the plasticizer is chemically bound. Internally plasticized copolymers would be expected to be superior to resins plasticized in the usual way in that the plasticizer cannot migrate, evaporate or cause unpleasant odors.

Emulsion copolymers of vinyl acetate with vinyl stearate are being used as water-base paints for outdoor applications. Polyvinyl acetate emulsions were among the first water-base paints to be examined, particularly for outdoor use, but problems concerned with external plasticization of the polymer and poor water resistance were discouraging factors. Internally plasticized copolymers of vinyl acetate with vinyl stearate overcome both problems satisfactorily.¹⁶

Copolymers of vinyl stearate with vinyl chloride fall into two main categories.¹⁷ Those containing about 10-20% of vinyl stearate are essentially rigid plastics. They may be advantageous for rigid plastic uses

where their low milling temperature and low viscosity-temperature coefficient are desired. Applications which suggest themselves are plastic tubes, pipes and other extruded forms, sheets for structural purposes such as floor coverings and wall board, and other uses such as toys and phonograph records.

Copolymers containing about 30-45% vinyl stearate resemble polyvinyl chloride resins plasticized externally with about 25-35% plasticizer. These polymers should be of particular advantage where plasticizer loss by migration, extraction or evaporation must be avoided or elimination of odors is desirable. Applications which suggest themselves are wire coatings including protective sheathing for coaxial cable, fabric and other protective coatings, especially those which are subjected to repeated wiping or washing of such as table covers and automobile seat covers, and in food packaging.

Vinyl chloride-vinyl stearate copolymers form flexible films and they can be plasticized if desired with the conventional plasticizers for polyvinyl chloride, as well as with less expensive plasticizers readily prepared from fats with which the copolymers, unlike polyvinyl chloride, are compatible.

Obviously only a small fraction of the interesting chemical reactions and uses of fatty acids could be described in this article. No mention has been made of recent work on the preparation of fatty acids containing fluorine, sulfur and phosphorus, nor of recent work in the addition of numerous reagents to the double bonds of unsaturated fatty acids. The increased research activity in this field will undoubtedly result in many significant developments in the near future both in fundamental and industrial chemistry.

REFERENCES

1. Prileschajew, N., Ber. 42, 4811 (1909); J. Russ. Phys. Chem. Soc. 42, 1387 (1910); ibid. 43, 609 (1911); ibid. 44, 613 (1912).
2. Swern, D., Chem. Reviews 45, 1 (1949); Chapter 7 in "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., N. Y. (1953).
3. Niederhauser, W. D. and Koroly, J. E., U. S. Patent 2,485,160 (1949).
4. Gall, R. J. and Greenspan, F. P., Ind. Eng. Chem. 47, 1147 (1955).
5. Witnauer, L. P., Knight, H. B., Palm, W. E., Koos, R. E., Ault, W. C., and Swern, D., Ind. Eng. Chem. 47, 2304 (1955).
6. Roe, E. T., Schaeffer, B. B., Dixon, J. A., and Ault, W. C., J. Am. Chem. Soc. 66, 1924 (1944); J. Am. Oil Chemists' Soc. 24, 45 (1947).
7. Mack, C. H. and Bickford, W. G., J. Org. Chem. 18, 686 (1953).
8. Knight, H. B., Koos, R. E. and Swern, D., J. Am. Chem. Soc. 75, 6212 (1953); J. Am. Oil Chemists' Soc. 31, 1 (1954).
9. Teeter, H. M., Gast, L. E., Bell, E. W. and Cowan, J. C., Ind. Eng. Chem. 45, 1777 (1953).
10. Hilditch, T. P., "The Chemical Constitution of Natural Fats," John Wiley and Sons, Inc., N. Y. (1944).
11. Bickford, W. G., Fisher, G. S., Kyame, L. and Swift, C. E., J. Am. Oil Chemists' Soc. 25, 254 (1948); Bickford, W. G., Krauczunas, P. and Wheeler, D. H., Oil and Soap 19, 23 (1942).
12. Teeter, H. M., Geerts, M. J. and Cowan, J. C., J. Am. Oil Chemists' Soc. 25, 158 (1948).
13. Bickford, W. G., Dupre, E. F., Mack, C. H. and O'Connor, R. T., J. Am. Oil Chemists' Soc. 30, 376 (1953). Paschke, R. F., Tolberg, W. and Wheeler, D. H., ibid. 30, 97 (1953).
14. Wheeler, D. H., Official Digest Federation Paint and Varnish Clubs, 322, 661-668 (1951).
15. Swern, D. and Jordan, E. F., J. Am. Chem. Soc. 70, 2334 (1947). Craig, L. E., Kleinschmidt, R. F., Miller, E. S., Wilkinson, J. M., David, R. W., Montross, C. F. and Port, W. S., Ind. Eng. Chem. 47, 1702 (1955).
16. Port, W. S., Kincl, F. A., and Swern, D., Official Digest Federation, Paint and Varnish Clubs 353, 408 (1954).
17. Port, W. S., Jordan, E. F., Palm, W. E., Witnauer, L. P., Hansen, J. E. and Swern, D., AIC-366, U. S. Department of Agriculture (1953).