Some New Aspects of Fatty Acid Chemistry

DURING the past 20 years, there has been a remarkable resurgence in the interest and research effort devoted to a study of the chemistry of fatty acids and their derivatives. This is a gratifying phenomenon since the chemistry of fatty acids represents one of the original areas of study in the chemistry of natural products, having been investigated in some detail by Chevreul approximately 150 years ago.

In a short paper, it is manifestly impossible to cover any significant number of the important aspects of the subject of fatty acid chemistry which have been ripening during the past two decades. I have decided therefore to discuss those new aspects of fatty acid chemistry which my colleagues and I have been studying for the past few years. Selection of the work of our own laboratory is not intended to convey the impression that the Eastern Regional Laboratory is the only place in which the newer aspects of fatty acid chemistry are being developed.

Some twenty-odd years ago, four regional research laboratories were established, one in each of the major crop-producing regions of the United States. These are known, respectively, as the Northern, Eastern, Southern and Western Regional Research Laboratories. One of the major objectives of these laboratories was, and still is, to find industrial uses for farm surpluses by chemical modification. One commodity which had a large surplus at that time and is with us in ever increasing quantities, is that of the inedible animal fats, notably tallows and greases, products assigned to the Eastern Laboratory. The inedible animal fats, in common with certain other agricultural surpluses, are by-products of another important industry, namely, the meat packing industry. Their availability, therefore, is rather intimately associated with man's increasing desire to eat meat; thus, their supply is not readily controlled, and the surplus is a more or less inevitable one; and an increasing one.

Considerable effort has gone into attempts to keep the surplus of fats as low as possible through chemical and other kinds of research. The Animal Fats Products Laboratory of the Eastern Regional Research Laboratory has been largely responsible for the chemical research in this area. Some of the more successful chemical developments from this group of our laboratory include expoxidised oils and esters; inedible animal fats in feeds; substitution of partially hydrogenated tallow for palm oil in the hot dip tinning of steel; preparation and polymerisation of vinyl stearate; and a process for the preparation of a purified oleic acid. This is far from a complete list, but I do not intend to mention older work at this time.

Finding new chemical uses for surplus agricultural commodities is important not only to reduce their surplus, but to provide an important, recurring industrial resource.

The bedrocks of the chemical industry of the United States are, of course, petroleum and coal chemicals. The great upswing in the use of these nonrecurring natural resources to produce organic chemicals did not occur until methods were available for obtaining the components of these raw materials in reasonably pure form. When these pure chemicals became available, the chemist was able to devise suitable reactions for converting them into useful materials. Billions of pounds of useful chemicals and products are now obtained from petroleum and coal chemicals. To cite just one example there is little doubt that without highly purified starting materials the polymer industry as we know it would not be in existence today.

On the other hand, a great deal of work on the conversion of fats to useful chemical derivatives has been applied to the fats themselves. It is well known that natural fats and oils are relatively complex mixtures of many substances and are not identical from batch to batch. The inevitable conclusion from this is that fats and oils cannot be expected to become important raw materials for the chemical industry, in the same sense that we think of petroleum and coal chemicals, unless and until the fats and oils can be separated into functionally pure entities. This purification, naturally, must be done at low cost; but when this is accomplished fats and oils can be expected to take their place with petroleum and coal chemicals as the third important source of industrial organic chemicals. We do not know when this day will come; when it does, however, there will be a true "oleochemicals" industry.

The approach which our research group has taken for the past 20 years in attempting to develop new and useful derivatives from inedible animal fats is to start with the fatty acid components of fats or their simple functional derivatives. To the research chemist this is certainly the only approach which is satisfying in

*Eastern Utilisation Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

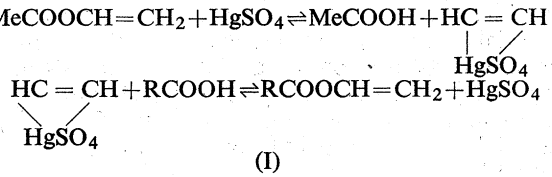
the long run, and we are convinced that it is the only long range approach of enduring value. Furthermore, it makes the problems much simpler to restrict one's efforts to substances whose composition is not only known with certainty but which are reproducible from day to day.

The work described deals with chemical reactions on highly purified substances. It is evident that some of the reactions are adaptable to the more complex mixtures presently available in commerce. Perhaps these reactions are not yet applicable to the cheapest raw materials, the fats themselves, but by having these reactions available, by knowing reaction conditions, yields, and methods of isolating components, by understanding the physical and chemical properties of the products, we may ultimately be able to extend these reactions to less expensive starting materials.

In this lecture, I propose to describe some recent research being conducted in the Exploratory Reactions Group of our laboratory by Dr. Edward S. Rothman, Dr. Leonard S. Silbert and Dr. John S. Showell.

Acid Catalysed Interchange Reactions of Carboxylic Acids with Enol Esters

The first reaction is that between vinyl acetate or isopropenyl acetate and carboxylic acids. Relatively little is known about the reactions of enol esters with long chain fatty acids. As shown (I) the reaction of vinyl acetate with carboxylic acids has been reported to be specifically catalysed by mercuric salts operating through an acetylenic intermediate and to be unaffected by sulphuric acid catalysis.

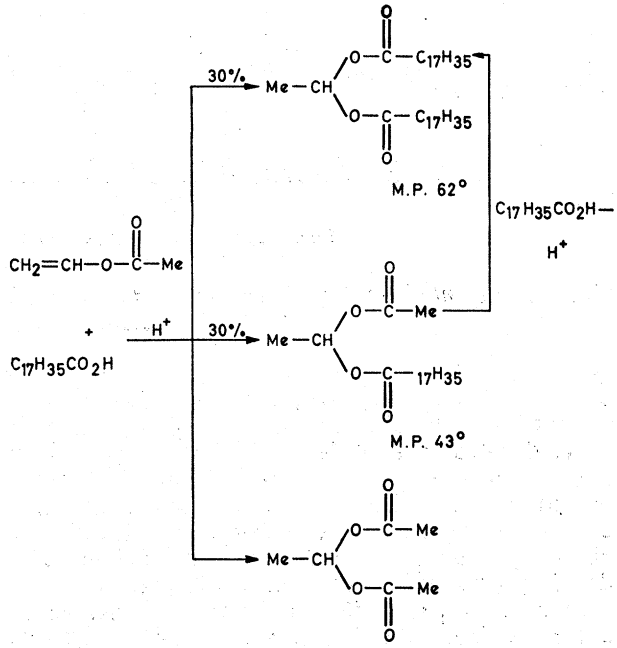


(I)

In contrast to this conclusion, it has been found that the reaction of vinyl acetate with stearic acid, using sulphuric acid as catalyst without mercuric salts present, leads to product formation. Adelman,[1] depending on titrations measuring liberated water-soluble acetic acid, believed no reaction occurred in the case of capric acid-vinyl acetate-sulphuric acid systems. In agreement with this work it was found that a water-soluble acid is not formed, and if the only criterion of reactivity was the formation of a water-soluble acid, we too would have concluded that sulphuric acid is an ineffective catalyst in the reaction of water-insoluble fatty acids with vinyl acetate.

As shown (II) the reaction of stearic acid with vinyl acetate in the presence of sulphuric acid produces three acylals: ethylidene distearate, ethylidene monostearate monoacetate, and ethylidene diacetate, as well as a small amount of an unidentified liquid acetate ester.

Ethylidene distearate, m.p. 62° was identified on the basis of (*a*) its infrared absorption spectrum which showed bands suggesting an acylal structure; (*b*) the absence of acetoxy bands; (*c*) saponification which gave the calculated amount of stearic acid per gram



(II)

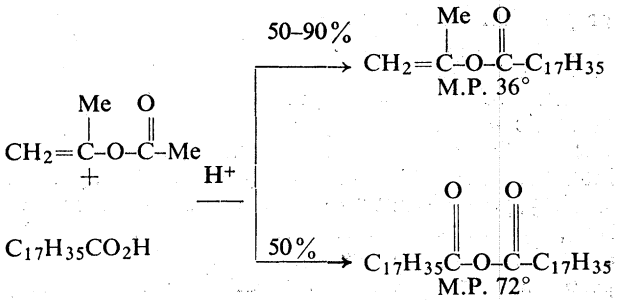
of ester on the assumption that the structure was ethylidene distearate; (*d*) the molecular weight value observed, approximately 580 grams per mole, in excellent agreement with the calculated value and (*e*) the *X*-ray long spacing and elemental analyses which were also in excellent agreement with the anticipated values.

The second major component of this reaction, ethylidene monoacetate monostearate, m.p. 43–46°, was identified on the basis of (*a*) the presence of a strong acetate absorption band in the infrared; (*b*) the *X*-ray long spacing value of 27·5 A which was of the right order of magnitude; (*c*) the elemental analyses which agreed well with calculated values; (*d*) the observed molecular weight determinations of approximately 350–400 which agreed reasonably well with the calculated value, and (*e*) conversion of ethylidene monoacetate monostearate to ethylidene distearate by reaction with stearic acid.

The yields of ethylidene distearate and ethylidene monoacetate monostearate are approximately 30%. Two other products which were identified are ethylidene diacetate, and some unreacted vinyl stearate.

Isopropenyl acetate, although the next higher homologous enol acetate reacts in an entirely different manner from vinyl acetate with stearic acid (and other fatty acids) in the presence of strong acid catalysts (III).

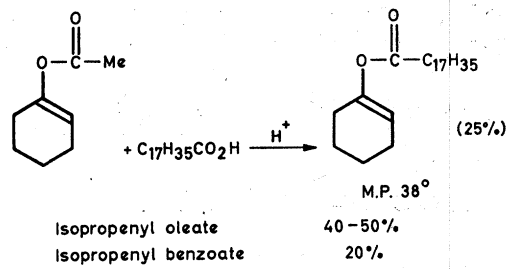
Refluxing an excess of isopropenyl acetate with stearic acid catalysed by sulphuric acid gives approximately equimolar amounts of two products, isopropenyl stearate and stearic anhydride. Since we believe that these reactions are equilibrium reactions, we decided to study the effect of added stearic anhydride to the isopropenyl acetate-stearic acid reaction mixture. When stearic anhydride was present initially in the reaction mixture, the yield of isopropenyl stearate (based on stearic acid converted)



(III)

rose from 53% (anhydride initially absent) to 68% when half a mole of stearic anhydride was present per mole of stearic acid and to 93% when one mole of stearic anhydride per mole of stearic acid was present.

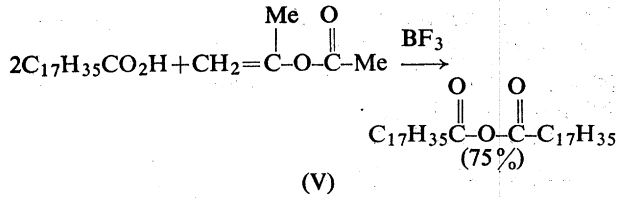
In view of the difference in behaviour of the homologues, vinyl acetate and isopropenyl acetate, toward stearic acid under conditions of sulphuric acid catalysis, it was decided to test the reactivity of the cyclic enol ester, cyclohexenyl-1-acetate, under the same conditions. As shown in (IV) a 25% yield of the interchange product, cyclohexenyl-1-stearate was obtained together with some stearic anhydride.



(IV)

In reaction of isopropenyl acetate with acids other than stearic acid, the following results were obtained. Oleic acid gave a 40–50% yield of isopropenyl oleate, whereas benzoic acid gave only a 20% yield of isopropenyl benzoate. Reaction of isopropenyl acetate with 9,10-epoxystearic acid and azelaic acid, respectively, yielded polymeric products.

One last interesting observation concerning the reaction of enol acetates with fatty acids should be made. As shown (V) the reaction of stearic acid with isopropenyl acetate in the presence of boron trifluoride and mercuric acetate gave an excellent yield of stearic anhydride directly. This procedure, then, should be a simple one for preparing fatty acid anhydrides from a wide range of fatty acids.

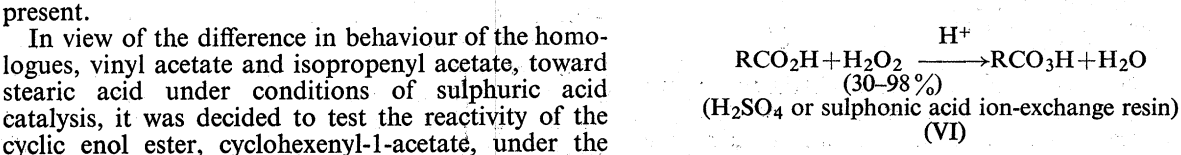


(V)

The characteristics of the various enol esters that we have prepared have not yet been examined. Our main point in describing this work is to describe a new field of activity currently being studied because we are interested in it and the chemistry is largely unexplored. In a year or two more information may be available on what these products can do.

Direct Preparation of Aliphatic and Aromatic Peroxy Acids

Peroxy acids have been known for about 50 years, but until very recently there was no general method for their preparation, applicable to saturated and substituted aliphatic acids and to substituted or unsubstituted aromatic carboxylic acids. To review briefly, water-soluble peroxy acids can be readily prepared by the acid catalysed reaction of the corresponding carboxylic acid with hydrogen peroxide in the equilibrium reaction shown (VI).



(VI)

This is by far the best procedure for making these peroxy acids, but the reaction is unsuccessful when the carboxylic acid is insoluble in aqueous hydrogen peroxide.

Several years ago it was shown by investigators in our laboratory that water-insoluble peroxy acids can be readily obtained if the reaction is carried out in concentrated sulphuric acid as the solvent-reaction medium and not merely in the presence of catalytic quantities. In this way, excellent yields of aliphatic monoperoxycarboxylic acids, through peroxypalmitic acid (C_{16}), and various diperoxy acids were obtained. The method was unsuccessful in the preparation of peroxystearic acid, owing to the insolubility of stearic acid in concentrated sulphuric acid, and the usual result was excessive decomposition and carbonisation. With aromatic carboxylic acids and certain substituted aliphatic carboxylic acids, peroxy acids could not be obtained either.

Since acid catalysis appears to be necessary in the direct preparation of peroxy acids from carboxylic acids, it was thought that methanesulphonic acid might serve as an excellent replacement for concentrated sulphuric acid. Methanesulphonic acid is readily available, it is a strong acid, it has better solvation capacity than sulphuric acid for organic compounds, and it does not have the oxidation-sulphonation possibilities that sulphuric acid does. To our pleasant surprise, methanesulphonic acid turned out to be an excellent reaction medium-solvent for the preparation of peroxy acids from water-insoluble aliphatic and aromatic carboxylic acids and from carboxylic acids which contained certain sulphuric acid-labile substituents. For the first time, it was possible to prepare aromatic peroxy acids directly from a wide variety of aromatic carboxylic acids by reaction with concentrated hydrogen peroxide in methanesulphonic acid medium. Table I lists some of the aromatic peroxycarboxylic acids prepared, their yields and melting points.

Table I

	Aromatic Peroxy Acids	
	Yield %	*M.P.*
peroxybenzoic	85–95	41–2°
p-t-butylperoxybenzoic	85	81·5°
p-nitroperoxybenzoic	95	138° (dec.)
o-nitroperoxybenzoic	75	95°
diperoxyterephthalic	93	—
p-cyanoperoxybenzoic	75	126°

Table II lists some aliphatic peroxy acids prepared by the methanesulphonic acid procedure.

Table II

	Aliphatic Peroxy Acids	
	Yield %	*M.P.*
peroxylauric	97	50°
peroxypalmitic	95	61°
peroxystearic	90	65°
12-hydroxyperoxystearic	90	62°
α-bromoperoxystearic	85	41°
α-bromoperoxycapric	85	—
diperoxysebacic	92	93°

Note that some of these contain substituent groups which prevented the formation of the peroxy acid when concentrated sulphuric acid was used as the reaction medium, but with methanesulphonic acid excellent yields of the peroxy acid were obtained.

Table III shows the room temperature stability of some of the solid peroxy acids.

Table III

	Stability,	*%*	*Weeks**
	2	*4*	*8*
peroxybenzoic	63	34	2·5
p-t-butylperoxybenzoic	100	99+	99+
p-nitroperoxybenzoic	100	100	100
o-nitroperoxybenzoic	100	99	99
diperoxyterephthalic	99+	96	95
peroxylauric	99+	98	96
α-bromoperoxystearic	43	16	1

*Per cent of peroxy acid retained on storage of solid at 25°.

These data were obtained because it is frequently important to know how to store peroxy acids and, furthermore, it is important to have such information if one wishes to make formulations containing peroxy acids. The most stable peroxy acid we have yet seen is *para*-nitroperoxybenzoic acid.

The stability of peroxy acids appears to be related in part to their melting points. The low melting peroxy acids are, in general, much less stable than the higher melting ones. This kind of situation has also been observed in other classes of organic peroxides. For example, long chain diacyl peroxides which are relatively high melting solids are stable at room temperature for long periods of time (up to several years) whereas liquid diacyl peroxides may decompose very quickly within a few months. Apparently the lower melting compounds have enough kinetic energy at room temperature in the solid state to cause significant decomposition to occur, whereas the higher melting compounds have much less kinetic energy. This, of course, is an over-simplification, but in a general way is applicable.

Peroxy acids are important oxidising agents. As is well known, large quantities of peroxyacetic acid, prepared and utilised *in situ*, are employed in the preparation of epoxidised soybean oil and other long chain epoxy esters. Peroxybenzoic acid is one of the most important of the classical epoxidising agents. We do not know yet what utility these newer aromatic and aliphatic peroxy acids will have, but certainly those which have high stability may find some industrial use. In addition to its unusually high stability, *para*-nitroperoxybenzoic acid is an extremely rapid epoxidising reagent, causing double bonds to epoxidise at approximately 50 times the rate with peroxyacetic acid. This observation is quite interesting as it may permit the preparation of many oxirane compounds not otherwise attainable to the chemist. It is true that *para*-nitroperoxybenzoic acid is relatively expensive, but the fact that it will permit the preparation of these hitherto unavailable oxirane compounds suggests that it might find some immediate application where special kinds of oxirane compounds are desired.

In addition to their use as epoxidising agents, long chain peroxy acids may also be useful in the preparation of other compounds. Thus, as (VII) illustrates, Paquot[2] and co-workers have shown that thermal decomposition of long chain aliphatic peroxy acids in a solvent in the *complete* absence of oxygen causes a homolytic decomposition to occur with attendant loss of carbon dioxide and the formation of the alcohol with one less carbon atom than in the original carboxylic acid employed.

$$RCO_2H \rightarrow RCO_3H \xrightarrow{\Delta} ROH + CO_2\uparrow$$

$$R-\overset{O}{\overset{\|}{C}}-O-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-O.+.OH$$

$$R-\overset{O}{\overset{\|}{C}}-O. \longrightarrow R.+CO_2$$

$$R\cdot + R-\overset{O}{\overset{\|}{C}}-O-OH \longrightarrow ROH + R-\overset{O}{\overset{\|}{C}}-O.$$

(VII)

The first step is homolytic decomposition of the peroxy acid to the acyloxy radical ($RCO_2\cdot$). By loss of carbon dioxide, this yields an alkyl radical ($R\cdot$) which attacks another molecule of peroxy acid, again forming the acyloxy radical, and continuing the chain.

Yields from this decomposition reaction are relatively high (~80%) and it affords a way to obtain odd numbered alcohols with straight chains from the corresponding even numbered carboxylic acids by the reaction sequence illustrated in (VII).

Selective Expoxidation of Unsaturated Compounds

As indicated earlier, the most important use for peroxy acids is in the epoxidation of unsaturated compounds e.g.:

$$-\overset{|}{C}=\overset{|}{C}- + RCO_3H \longrightarrow -\overset{|}{C}-\overset{|}{C}- + RCO_2H$$

(or H_2O_2—RCO_2H)

In many cases, the epoxidation reaction is extremely rapid, but in many others the reaction proceeds quite slowly. Approximately 15 years ago, in a compilation of work carried out in our own laboratory and elsewhere, we published a paper[3] listing the relative rates of epoxidation of a wide variety of olefins of different structural types with peroxyacetic acid at 25°. These results are summarised in (VIII).

$CH_2{=}CH_2$	1
$Me{-}CH{=}CH_2$	25
$Me{-}CH{=}CH{-}Me$	500
$(Me)_2C{=}CH{-}Me$	6000
$(RCO_2)CH{=}CH(CO_2R)$	~ 0
$R{-}CO_2CH{=}CH_2$	<1

(VIII)

Thus electron-releasing groups attached to or in close proximity to the double bond cause an increase in the rate of epoxidation whereas electron-withdrawing groups cause a decrease in rate.

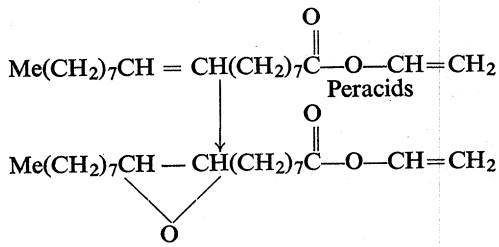
Rate Increase	*Rate Decrease*
Alkyl	Carbonyl
Alkyl	Carbonyl Ester
(Electron Release)	(Electron withdrawal)

Obviously, then, in the case of olefins containing more than one double bond with different substituent groups it should be possible to effect a selective epoxidation, provided that one double bond is epoxidised at a much more rapid rate than the other one present in the molecule.

This point is illustrated by the relative rates of epoxidation of vinyl laurate and vinyl oleate at 30° with perbenzoic acid.

Vinyl Laurate	1
Vinyl Oleate	200+

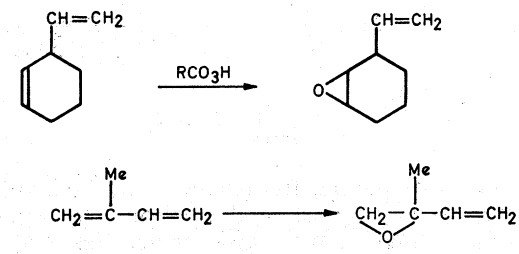
On the basis of the low rate of epoxidation of the vinyl double bond in vinyl laurate, compared with that of the internal double bond in vinyl oleate, it became clear to us that a selective epoxidation of vinyl oleate should be possible. This selective epoxidation was extremely successful, and the new monomer vinyl epoxystearate was obtained for the first time (IX).



(IX)

This monomer is interesting because it has a vinyl double bond which undergoes free radical polymerisation while maintaining the oxirane group intact. The soluble copolymer then obtained can be cured in the conventional way using typical oxirane curing agents.

Various other examples of this type of monomer (vinyl-epoxy) have been prepared in other laboratories; e.g. vinylcyclohexene monoepoxide.



(X)

The double bond in the cyclohexene ring, being a disubstituted double bond, is much more rapidly epoxidised than the external vinyl double bond.

Numerous other examples of this selective epoxidation could be given. One other example will suffice, namely, the partial epoxidation of isoprene, also illustrated (X). The double bond which epoxidises selectively is that double bond which has the electron-releasing methyl group attached to it.

The last example of selective epoxidation to be discussed involves a laboratory procedure for the preparation of very pure 1-olefins. Several years ago we became interested in the possibility of obtaining isomer-free terminal sulphonic acids from 1-olefins by the sequence of reactions shown, which involved addition of thiolacetic acid to the double bond followed by oxidation of the thiolacetate to the terminal sulphonic acid (XI).

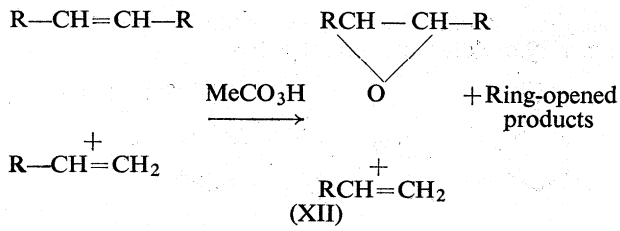
$$R{-}CH{=}CH_2 + MeCOSH \longrightarrow RCH_2{-}CH_2SCOCH_3 \xrightarrow{H_2O_2-HOAc} RCH_2CH_2SO_2OH$$

(XI)

The preparation of isomer-free aliphatic sulphonic acids is not an easy job by classical methods, and the sequence shown gives excellent overall yields from olefins. It was desirable, therefore, to have rigorously pure 1-olefin at hand. Free-radical addition of thiolacetic acid to terminal double bond systems goes almost exclusively (50–1000:1) to the terminal carbon atom, so we had a very convenient way to put the sulphonic acid group at the end of a chain provided we had the pure 1-olefins.

All samples of 1-olefins obtained commercially are contaminated with varying amounts of internal and/or branched chain isomers to the extent of as much as 15 or 20%. (The presence of these internal olefins can be shown by infrared analysis.) Since it was well known that an internal olefin epoxidises perhaps 20–30 times more rapidly than the terminal olefin as shown earlier, a selective epoxidation procedure was devised which epoxidises internal olefin with only a modest sacrifice of the 1-olefin (XII).

This involved reaction of equimolar amounts of olefin with peroxyacetic acid for a predetermined period of time to convert the internal olefin to epoxide, hydroxyacetate, glycol and polymer as a result of the workup procedure. The 1-olefin could



now be readily separated from these oxygen-containing materials, usually by steam distillation. A vacuum fractional distillation then gave isomer free 1-olefin in fair yield. Although this is a time-consuming procedure, it was the only procedure available to us for preparing rigorously pure, isomer-free 1-olefin.

In conclusion, therefore, we have attempted to describe three areas of research that are being conducted in our laboratory, namely, reactions of enol acetates with fatty acids, preparation of peroxy acids and selective epoxidation. There are many other interesting aspects of fatty acid chemistry which could be discussed, some of which are also in progress in our laboratory. These are not far enough along to be able to talk about them in any positive way. There is also considerably fine work being conducted in many other laboratories, both in the United States and abroad.

We believe fatty acids and their derivatives to be versatile raw materials which should be given considerably more attention by industry, and we are convinced that "oleochemicals" will someday take their proper place with petrochemicals and coal chemicals as the three most important sources of organic chemicals for a wide variety of industrial applications.

References

[1] Adelman, R. L., *J. org. Chem.* 1949, **14**, 1057
[2] Lefort, D., Paquot, C. & Sorba, J., *Bull. soc. chim. France* 1959, 1385
[3] Swern, D., *J. Am. Chem. Soc.* 1947, **69**, 1692