

THE ARALKYLATION, ALKYLATION AND ACYLATION OF OLEIC ACID

By

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Thesis submitted to the Faculty of the Graduate School  
of the University of Maryland in partial  
fulfillment of the requirements for the  
degree of Doctor of Philosophy

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### Acknowledgement

The author wishes to express his appreciation to Professor N. L. Drake of the University of Maryland and to Mr. P. H. Groggins and Dr. A. J. Stirton of the Industrial Farm Products Research Division, Bureau of Agricultural Chemistry and Engineering, for their advice and cooperation during the course of this work.

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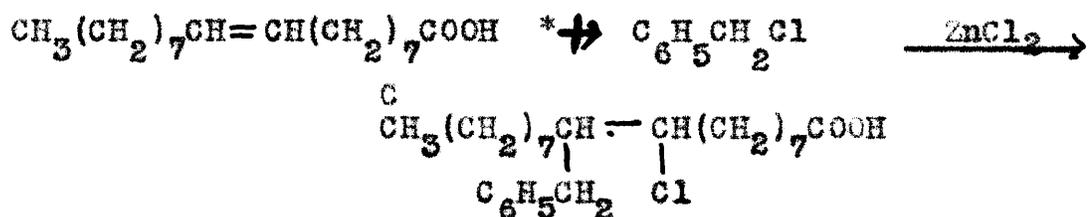
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## I INTRODUCTION

The purpose of this work was to test the applicability of reactions of the Friedel Crafts type in synthesizing alkyl- aralkyl- and acyloleic and stearic acids by the interaction of oleic acid and alkyl- aralkyl- and acyl halides in the presence of metallic halides. Acylation and alkylation of unsaturated hydrocarbons is a well established reaction, and because of the low cost of such reagents, any comprehensive program of research to explore the possible uses of oleic acid in organic synthesis should include these Friedel and Crafts syntheses. The arylation of oleic acid has been recently reviewed and the reaction extended to include preparation of many new arylstearic acids.(32) In the present investigation, however, the oleic acid as well as the acylating or alkylating agent are aliphatic compounds; furthermore there exists the possibility both of isolating the intermediate compounds formed by addition as well as the olefins formed by dehydrohalogenation. Addition compounds are assumed to be intermediates in the mechanism of various aromatic Friedel Crafts syntheses.

The relatively high molecular weight of oleic acid as well as the presence of the carboxyl group are responsible for some of the difficulties in applying these reactions of alkylation and acylation. In Friedel Crafts syntheses, benzyl chloride is one of the most reactive alkylating agents. If oleic acid behaved like ordinary hydrocarbon olefins,

the reaction with benzyl chloride would proceed as follows:

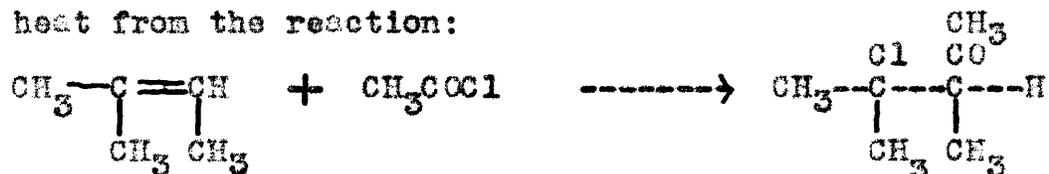


The product would be a mixture of the 9-(or 10-) chloro-10- (or 9-) benzylstearic acids, from which by a proper choice of reaction conditions hydrogen chloride can be split out. The resultant benzyloleic acid then could form a second addition product which would yield a disubstituted oleic acid by dehydrohalogenation. Whether this disubstituted acid would react further is problematical. The obstacle to these reactions is the reactions of oleic acid with metal chlorides, and the reactions of alkyl halides with themselves. (24) The reaction of acyl halides would follow along similar lines to give products in which another carbonyl group would be present, as ketochlorostearic acids. The reactive ketone group should present interesting possibilities for the synthesis of fat acid derivatives. The arylated stearic acids have been shown to give a new and potentially useful series of wetting agents by simple sulfonation. (52) New compounds resulting from the acylation-alkylation reaction might be of interest as addition agents to lubricants, notably as viscosity index improvers, compounds to improve film strength, and wear reducers. The chlorine containing addition products offer another possibility in that the chlorine should be replaceable to give sulfonic acid groups by reaction with alkali acid sulfites. Most of the newer wetting agents are similar combinations of long hydrocarbon chains and  $\text{SO}_3\text{H}$  groups.

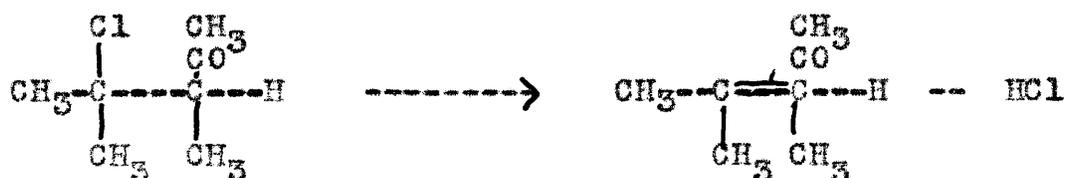
## II HISTORICAL

A reaction product formed by the action of benzyl chloride on oleic acid in the presence of zinc chloride, with subsequent sulfonation to produce a wetting agent, has been described in U. S. Patent 1,667,225. (34) However the product is merely described as a yellowish colored oil and no data is given on its properties. U. S. Patent 2,144,324 (6) also mentions a benzylated oleic acid, but gives no data on the product.

The acylation of oleic acid, as far as is known, has not been described in the literature. Addition of acyl halides to ethylenic linkages is a well authenticated reaction, known since Kondakow's work in 1892 (22) with trimethylethylene and acetyl chloride. No reaction occurs until a trace of zinc chloride is added, when there is a sudden evolution of heat from the reaction:



The chlorinated ketone may be made to disengage HCl by many reagents to give an unsaturated ketone:



In 1898 G. Blanc(5) used  $\text{AlCl}_3$  as a catalyst to promote the reaction of acetyl chloride and 1,1,2, trimethylcyclopentene-2.

S. Krapiw in 1908 (23)- reported yields of unsaturated ketones ranging from 20 to 40 percent using aluminum bromide

as a catalyst and working at 0-10°C with various olefins and acetyl bromide or chloride. He observed the formation of addition products, chloroketones, as well as chlorinated hydrocarbons.

From this time on the reaction was well authenticated, and large quantities of metallic halides were used, guided no doubt, by the need for stoichiometric quantities of  $AlCl_3$  in Friedel Crafts reactions involving acid halides and aromatic compounds. Darzens and Rost (13) used 250 grams of stannic chloride for each mole of acid chloride and worked below zero degrees Centigrade.

In 1939 Colonge and Mostafi (9) reviewed the earlier work and established the fact that small quantities of stannic chloride are the most effective catalyst, and extended the application to many ethylenic hydrocarbons. They were able to react acetyl chloride with tetramethylethylene and concluded that this established the reaction mechanism as addition, not a substitution followed by the addition of HCl to the double bond to give a chloroketone. They used five grams of stannic chloride to 0.5 mole of acid chloride, 0.75 mole of olefin, and worked at temperatures of 0-10° C. Yields of 65 percent were reported, in the case of 2-methylhexene-2 and acetyl chloride. Reaction times were limited to a few hours, after which the mixture was hydrolyzed with dilute hydrochloric acid, washed free of acid and then dried. It was possible to distill some of the beta-chloroketones without decomposition. If the unsaturated ketone was desired,

dehydrohalogenation was effected with dimethylaniline. A low boiling chlorinated olefin which had been formed by side reactions was distilled off under low pressure, and the remaining beta-chloro ketone was refluxed with an excess of dimethylaniline. The mixture was washed with dimethylaniline salts, and then washed free of acid, dried and distilled under low pressure to give a ketoolefin.

The alkylation of oleic acid has not been described in the literature. Straus and Thiel (33) discuss the addition of alkyl halides to the double bond, and carried out a series of addition reactions with alpha-methoxybenzyl chloride and alpha-methoxymethyl chloride. The hydrocarbons used by Straus and Thiel ranged from very reactive dienes to isobutylene and dihydronaphthalene. Straus and Thiel stated: "It has not yet been possible to add benzyl chloride in such additions", and that the methoxy group is needed to give the needed polarity for addition. They were able to make para anisyl chloride add to butadiene and cyclohexadiene in small yields. Tertiary chloride would not give the expected reaction product with butadiene, and only reacted with cyclohexadiene in the presence of large amounts of mercuric chloride to give a complicated product in which two molecules of the hydrocarbon were involved.

### III THEORETICAL

The theoretical evolution of heat in a reaction may be calculated from the bond energies involved. In general, a reaction which evolves a large amount of heat should take place spontaneously. The addition of a catalyst will affect the speed of the reaction, but not the amount of heat evolved.

In the alkylation, acylation and aralkylation of oleic acid, we may summarize the reactions as follows:

1 carbon-carbon double bond -- 1 carbon-chlorine bond ---

2 new carbon-carbon bonds -- 1 new carbon-chlorine bond.

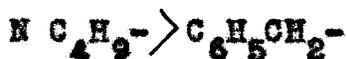
and, on the basis of the bond energies calculated by Pauling, (28) the equation reads:

150 Kg. Cal. + 78.6 Kg. Cal. ----> 2 times 83.7 Kg. Cal. + 78.6 Kg. Cal.

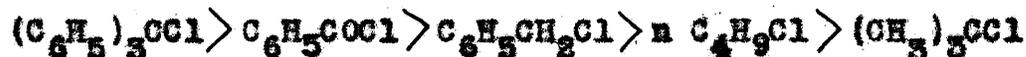
These figures show that there will be an evolution of heat in the addition reaction, equal to 246.00- 228.60 Kg. Cal. or 17.40 Kg. Cal. per mole of reactant olefin. The value given for the C--Cl bond is an average one, and will vary from compound to compound, depending on the nature of the atoms and groups attached to the other valencies of the carbon.

The effect of the groups attached to the C--Cl link is very complex and may not be considered as that of a simple electronegativity series, such as that given by Hurd (19), who gives the series, starting with the most electronegative:

p-CH<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>-> o or p CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-> C<sub>6</sub>H<sub>5</sub>-> CH<sub>3</sub>-> C<sub>2</sub>H<sub>5</sub>-> n C<sub>3</sub>H<sub>7</sub>->



We may refer to the measured relative reactivities of chlorides with potassium iodide. (10,11,12) Choosing those connected with this work, we have the following series:



To derive a reactivity series for the chlorides used in the present work, a gram mole of oleic acid was mixed with a gram mole of each of the chlorides, and then ten grams of stannic chloride was added with rapid stirring. From time to time, iodine numbers were determined on small samples of the mixture, and these iodine numbers were used to calculate the percentage of addition compound formed. The plot of these numbers is shown in Graph 1 and the actual figures are given below.

Table 1

Reactivity of various halides with Oleic acid.

Catalyst, 0.02 mole of  $\text{SnCl}_4$ .

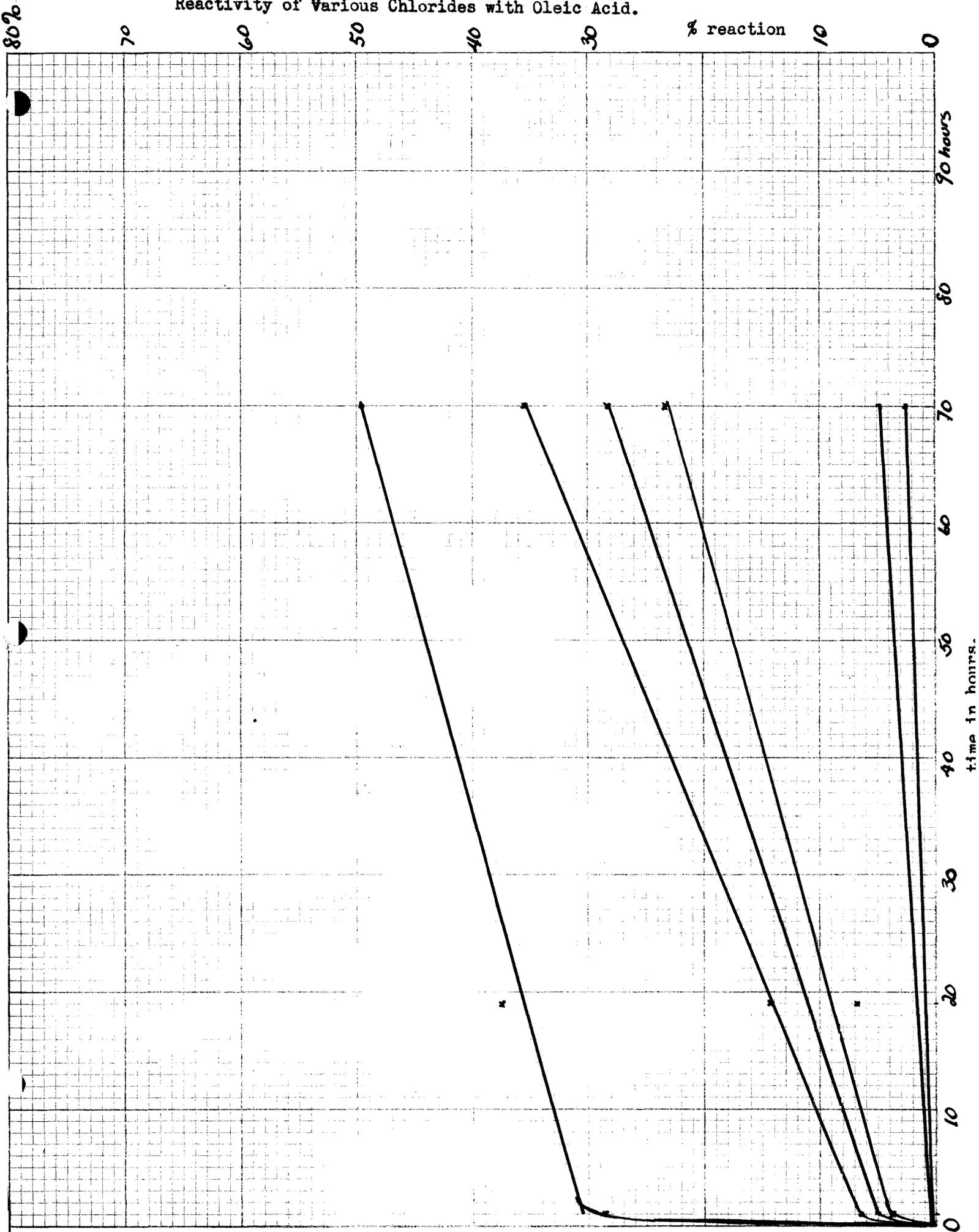
Room temperature.

Chloride	1 hour	19 hours	70 hours
Tert. butyl	--	1.6%	2.5%
n butyl	--	0.8%	4.9 %
benzyl	3.8%	6.8%	23.3%
$\alpha$ -methoxy-benzyl	6.4%	14.1%	35.6%
benzoyl	5.0%	---	28.2%
acetyl	28.7%	37.4%	49.3%

(--- indicated not determined)

It is evident from this table that the series given by the

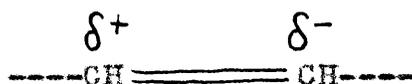
Reactivity of Various Chlorides with Oleic Acid.



percentage of addition compound at 70 hours,  
 acetyl chloride > alpha-methoxybenzyl chloride > benzoyl chlor-  
 ide > benzyl chloride > n butyl chloride > tertiary butyl  
 chloride, agrees with the reactivity of the chlorides toward  
 KI rather than the order of relative electronegativity.

Alpha-methoxybenzyl chloride was suggested by the re-  
 searches of Straus and Theil (33) who found this alkyl chlor-  
 ide added rapidly to the double bonds in cyclohexadiene and  
 cyclopentadiene, and to a lesser extent in dimethylethylene,  
 trimethylethylene, butadiene and isobutylene. These olefins  
 are of low molecular weight, and the grouping  $>C=C<$  consti-  
 tutes a greater porportion of the molecule than it does in  
 oleic acid. The negative effect of the carboxyl group on addi-  
 tions to the double bond is shown in the case of the alpha-  
 beta- unsaturated acids, which will not give an iodine number  
 with the usual reagents.

The addition to a double bond may be considered to be de-  
 pendent first on an activation of the double bond(36);

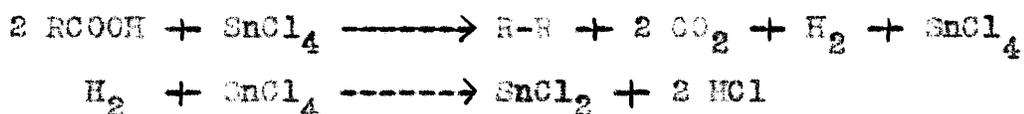


indicating an electronic displacement, momentary in nature,  
 but providing a point of attraction for the dipole existing  
 in the halide. We note that in the KI reaction series, that  
 those halides showing the greatest reaction speeds are those  
 considered the most polar. The two molecules associate more  
 closely until the actual bonds are broken and the new addi-  
 tion compound is formed. The ease with which this new com-  
 pound is formed is of course dependant on the ease with which  
 the old bonds may be broken, and with the halide this appar-

ently corresponds with the ease of ionization in ionizing solvents.(33) The acyl halides react vigorously with water, alpha-methoxybenzyl chloride may be titrated with N/10 NaOH, and benzyl chloride may be titrated in hot solution.

Straus and Theil did not believe that benzyl chloride could be made to react with olefins, but p-methoxybenzyl chloride was shown to give small yields of the addition compound. Placing the methoxyl group on the alpha carbon, as in alpha-methoxybenzyl chloride activates the carbon still further, and larger yields are obtained.

An objection may be raised to the use of iodine numbers as a means of following these addition reactions. Reaction of the carboxyl group of oleic acid with the double bond would result in a lowering of the iodine number, as well as any association of the double bonds of two molecules. The work of Chowdhury and coworkers (7) is a partial answer to this question. They were unable to detect any such reactions in oleic acid reacted at temperatures up to 100°C with SnCl<sub>4</sub>, but did conclude that the main reaction might be expressed:



The hydrogen also reacted with oleic acid to give stearic acid, which was isolated by centrifuging out the acid from the reaction mixture. This lowered the iodine number. If the reaction between the oleic acid and the halide is slow, the products formed by the reaction of the oleic acid and the catalyst become important. Benedikt(4) reacted ten parts of

oleic acid and one part of zinc chloride at 185°C until a test portion became solid on cooling. Analysis showed the following products:

Liquid anhydride	8%
Stearolactone	28%
Hydroxystearic acid	17%
Oleic acid isomers	40%
Saturated acids	<u>7%</u>
	100%

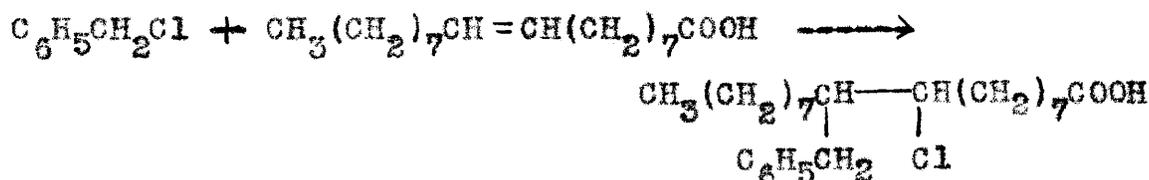
However most of this is based on calculations from iodine number, acetyl number, and saponification value, and the only compounds actually isolated were stearolactone and oleic acid isomers.

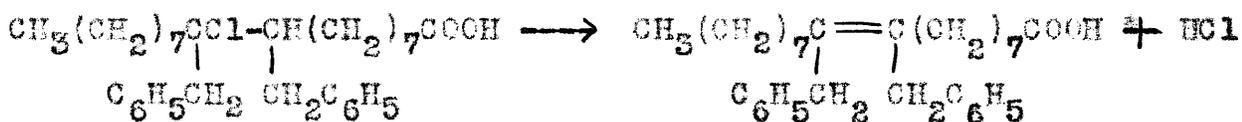
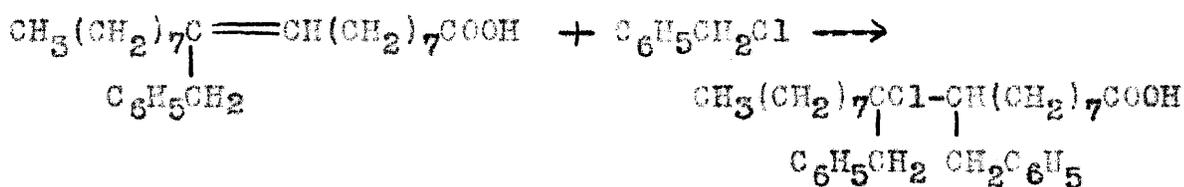
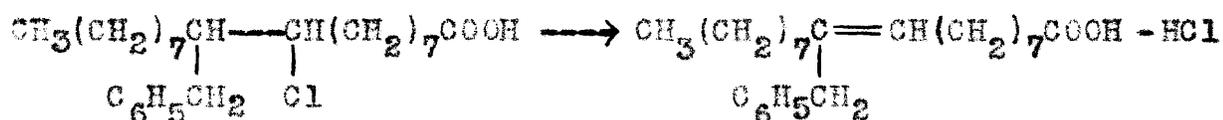
Bauer and Panagoulas (3) isolated 10-11 oleic acid and a hydroxystearic acid from the reaction products of zinc chloride and oleic acid in acetic acid solution.

One possible means of inhibiting the polymerization reactions lies in the use of esters of oleic acid. Chowdhury (7) has shown that stannic chloride has less polymerizing effect, as shown by iodine number and acid number determinations, on esters than on the acid.

#### Alkylation

In the present research problem, the following mechanism is suggested for the benzylation of oleic acid:



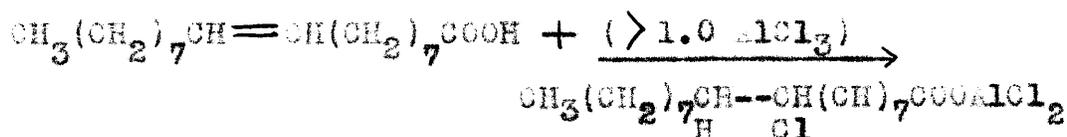


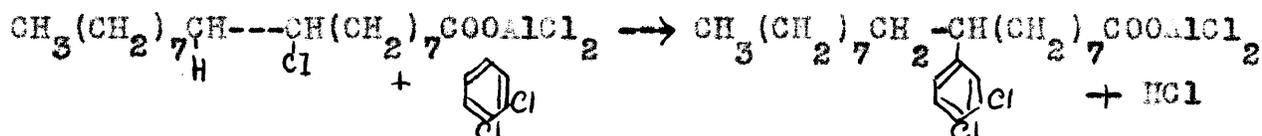
Owing to the instability of the chloro compounds at 150°C, the addition compounds split off HCl and form the unsaturated aralkylated compound. . . dibenzylated oleic acid is the most highly aralkylated form isolated, and no evidence for tri-benzylation has been obtained.

Low temperature experiments at 50-80°C give a chlorine containing acid with a low iodine number, but attempts to purify this by distillation always resulted in the breaking out of HCl. No monobenzyloleic acid has been isolated by distillation methods, even if the reaction product was treated with dimethylaniline to remove HCl. It is possible this compound is too reactive to exist where there is an excess of benzyl chloride present.

#### Alkylation

The alkylation of oleic acid in orthodichlorobenzene solution by butyl chloride has not given any alkyloleic or alkylstearic acids. Instead an estimated 35% of the reaction product has been shown to be 3,4-dichlorophenylstearic acid. The suggested mechanism for its formation is:

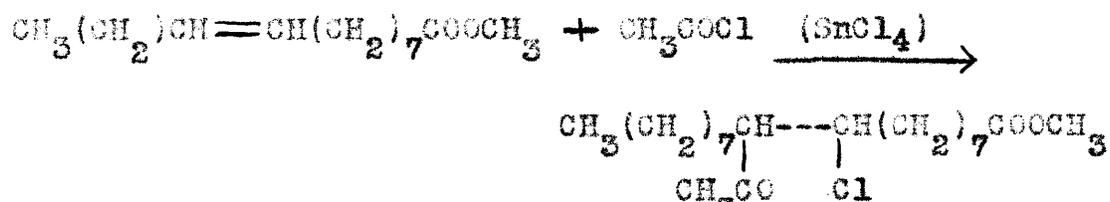




The  $\text{AlCl}_2$  attached to the carboxyl group is removed in the hydrolysis of the reaction product. Of course, the reaction may take place as well at the 10 as the 9 position, so that the product is a mixture of the two isomers. (17) Although butyldichlorobenzenes are present in the reaction product before the purification of the 3,4-dichlorophenylstearic acid, no butyldichlorophenylstearic acid was isolated.

#### ACYLATION

No acetyloleic or acetylstearic acids have been isolated from the reaction of acetyl chloride and oleic acid. Methyl acetylchlorostearate has been isolated from the interaction of methyl oleate and acetylchloride. Its formation would follow the same course as the formation of the first product in the benzylation mechanism:

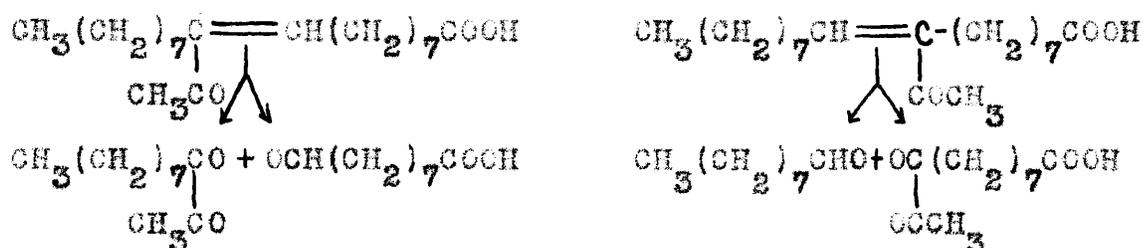


This methyl acetylchlorostearate<sup>3</sup> could be dehydrohalogenated to give methyl acetyloleate. The ester would be a mixture of the 9 and 10 isomers.

#### STRUCTURE

Harmon and Marvel (17) proved that phenylstearic acid, when made by the reaction of oleic acid with benzene in the presence of aluminum chloride, was a mixture of the 9 and 10 isomers. The same possibility exists in these reactions; in

all probability the product will be a mixture of the two isomers. However no attempt has been made to prove the relative amounts. In the cases where an unsymmetrical compound is produced by dehydrohalogenation, as e. g., acetyloleic acid, it might be expected that the compound could be isolated to a glycol which could then be split by periodic acid. The relative yields of the two scission products would reflect the proportions of the two isomers in acetyloleic acid:



Attempts were made to carry out this type of scission on dibenzoyloleic acid, but were unsuccessful.

After careful fractionations had produced materials believed to be dibenzoyloleic acid and 3,4-dichlorophenylstearic acid because of their analysis and physical properties, the final proof was accomplished by means of potassium permanganate and chromic acid oxidations. The first compound gave benzoic acid on oxidation with permanganate, and the second compound gave 3,4-dichlorobenzoic acid when oxidized with sulfuric acid and sodium dichromate.

Molecular refractivities were calculated from the data given by Luvers and Eisenlohr. (2)

## IV EXPERIMENTAL

The materials used were the ordinary C.P. grades of reagent chemicals, except for a few special cases. The oleic acid used was the U. S. P. grade. However the requirements for this grade merely specify a minimum iodine number, and a solidification point test for the relative amount of stearic acid.(35) To check on the purity of the oleic acid, iodine number was determined by the Hanus method (1), thiocyanogen number by the method given in Jamieson (20) and the relative proportions of the various fat acids were calculated from these figures.

Table II

Composition of a U. S. P. grade Oleic Acid  
and a "C. P. Oleic Acid"

Acid tested	Iodine No.	Thiocyanogen No.	Calculated % composition		
			Oleic	Linoleic	Stearic
Oleic acid, U. S. P.	91.9	77.5	75	13	12*
Oleic acid "C. P."	88.8	80.0	79	10	11*

\*This figure included unsaponifiable material when calculated from the iodine and thiocyanogen numbers.

To verify these estimates, nonsaponifiable materials were determined by the method given in Jamieson (20) and stearic acid determined by the leadsalt-ether method of Twitchell (1), for the U. S. P. oleic acid. The stearic acid was determined at 3.40 percent and the unsaponifiable material amounted to 3.75 percent. Considering that the iodine number of the remaining fat acid mixture would be raised by the presence of

linoleic acid, we see that the purity of the oleic acid may be estimated as high as 86 percent when determined by the more direct chemical method. Calculations based on two analytical values may of course cause the resultant figure to be in error by the sum of the individual errors.

#### GENERAL METHODS

The conditions under which the benzylations were carried out varied, but the yield estimates were based on a distillation. After the reaction, as determined by the lowering of iodine number, had run its course, the product of one gram mole of oleic acid was hydrolyzed with 200cc of 15 percent hydrochloric acid, followed by washings with distilled water until neutral and dried with anhydrous sodium sulfate. When an analysis showed that large amounts of chlorine were present in the product, the dried oil was refluxed with twice the theoretical amount of dimethylaniline for two hours. After cooling, the excess dimethylaniline and its salt were removed by extraction with dilute hydrochloric acid, followed by washing with distilled water until neutral. The oil was again dried with anhydrous sodium sulfate. Sometimes to facilitate the separation of the water, the oily material was taken up in an equal amount of ether. The last step after drying was then the removal of ether by vacuum on the steam bath. Now the material could be vacuum distilled at high temperatures without disengaging hydrogen chloride.

Acylation experiments were handled similarly to the benzylation experiments. In the earlier experiments the hydrogen chloride was not always removed by chemical means and began

to lower the vacuum when the temperature of the distillate approximated 180°C.

After fractionation, the various fractions of acid were analyzed by standard procedures for iodine number, saponification equivalent, neutralization equivalent, percentages of chlorine, and acetyl number. The procedures used were those found in the Association of Official Agricultural Chemists' latest yearbook (1). Chlorine was determined by sodium peroxide fusions in the Parr bomb.

The distillations were conducted in all glass equipment with standard taper ground glass joints. The retort flasks and columns were electrically heated and regulated by auto-transformers.

## ARALKYLATION

### EXPERIMENTS WITH BENZYL CHLORIDE

It was decided to follow the benzylation of oleic acid with benzyl chloride as far as possible by analytical means. One mole of benzyl chloride, one mole of oleic acid, and five grams of freshly fused zinc chloride were placed in a three necked flask equipped with a stirrer, thermometer, and reflux condenser. The heat was slowly raised to 150°C, where it was held for the duration of the run. The following table III contains a summary of the experiment. It may be noted that the neutral equivalent fluctuated slightly, possibly due to the varying amount of dissolved hydrogen chloride in the mixture; the saponification equivalent slowly rose, due to the disappearance of free benzyl chloride which reacts with 0.5 normal potassium hydroxide. The iodine number decreased

TABLE III  
 BENZYLATION OF OLEIC ACID  
 COURSE OF THE REACTION

Elapsed time (minutes)	Temp. °C	Neutral Equiv.	Saponif. Equiv.	Iodine No.	Chlorine (%)
0	28	400	---	63.5	9.10
15	72	395	236	65.8	8.51
30	140	379	251	40.1	8.63
60	140	383	362	18.8	5.55
90	135	384	358	20.0	5.33
120	150	389	355	21.6	4.63
150	150	401	364	16.3	4.38

(No hydrogen chloride was evolved until the temperature reached 72°C, at which time a few bubbles could be seen rising. When the temperature reached 140°C, a vigorous evolution of hydrogen chloride took place, and the benzyl chloride began to reflux. This rapid evolution of hydrogen chloride continued for about 3 hours, at which time the refluxing of the benzyl chloride began to decrease. At the end of the experiment the evolution of hydrogen chloride was only slight.)

regularly. In accordance with the evolution of hydrogen chloride, the chlorine content of the mixture decreased.

The dark oil resulting from the reaction was washed with dilute acid and water to remove the zinc chloride remaining in the mixture. The oil was dried at  $110^{\circ}\text{C}$  overnight, and then treated with dimethylaniline, refluxing at  $250^{\circ}\text{C}$  for two hours to remove chlorine. This removed the chlorine which would otherwise evolve as hydrogen chloride during the distillation. Excess dimethylaniline and its salts were removed by acid followed by water washes until the washings were neutral. The crude oil now had an iodine number of 40.6 (increase of 24.3 units) and a neutral equivalent of 516. It was now given a vacuum fractionation, summarized:

#### Distillation 1

Fractionation of 251 grams of reaction product.

Fraction	Boiling range ( $^{\circ}\text{C}/\text{mm.}$ )	Wt. Frac. (g.)	% frac.	N. E.	$\text{I}_2$ No.
I	150-180/0.1	60	23.9	347	55.6
II	180-220/0.2	70	27.9	402	53.1
III	250-310/0.5	39	11.6	443	41.1
Residue.		82	33.9	1042	22.2

Here the neutral equivalents show a steady rise with distillation temperature. The lower fractions are near the equivalent of oleic acid (N. E. 202) and rise steadily to that of the last distilled fraction, which happens to have the same neutral equivalent as the theoretical dibenzyleoleic acid. The residue in the flask has a very high neutral equivalent, and is partly insoluble in the alcohol solvent used to

determine neutral equivalent. During the distillation there was no marked accumulation of any fraction at a given temperature, so it was decided to distill larger amounts of the benzylated acids to get material for structure proof.

In accordance with the procedure of U. S. Patent 1,667,225 (34) which details the supposed preparation of dibenzyloleic acid, two moles of benzyl chloride, one mole of oleic acid, and five grams of zinc chloridewere heated at 150°C for four and one half hours, after which the oil was washed with dilute hydrochloric acid and water to remove the catalyst. The oil was taken up in ether, driedwith sodium sulfate, and the ether removed. Chlorine was determined gravimetrically with the aid of a Parr bomb at 2.66percent. Dimethylaniline was used to remove this chlorine, and the excess removed by washing with hydrochloric acid. The oil was dried and then vacuum distilled:

Distillation 2

Fractionation of 472 grams of reaction product,  
from benzylation at 150°C

Fraction	Boiling range. (°C/mm.)	Wt. Frac. (g.)	% Frac.
I	150-250/0.1	119	25.2
II	250-340/0.1	62	13.1
Residue.		249	52.8

After this preliminary fractionation, it was decided to analyze the residue which amounted to such a large percentage of nondistillable matter, in order to determine its nature. A chlorine determination showed that only a trace of chlorine was present. A carbon and hydrogen determination

gave check values, 87.3 and 87.4 percent carbon, 8.60 and 8.55 percent hydrogen. These values showed that it was not a pure benzyl resin,  $(C_7H_7)_n$ , which would have the composition 92.3 percent carbon, 7.7 percent hydrogen, but about 30 percent of oleic acid polymers were mixed with the benzyl resin. (24)

To determine the nature of the semisolid, low neutral equivalent acids, fraction one of the last distillation was given a careful refractionation.

#### Distillation 3

Redistillation of low boiling acids, Frac I prev. distill'n.

Frac.	Boiling range	Wt. Frac.	% Frac.	N. E.	I <sub>2</sub> No.	S. E.
I	160-170/0.1	12	4.0	---	---	---
II	170-171/0.1	53	17.6	372	44.2	294.5
III	171-180/0.1	41	13.6	370	58.2	294.0
IV	180-217/0.1	23	7.6	316	---	---
V	217-250/0.1	19	6.3	475	---	---
VI	250-295/0.5	8	2.6	---	---	---
Residue.		7	2.3	---	---	---

These results show that a large part of the material which can be distilled has a saponification equivalent close to that of oleic acid, and because it is solid at room temperature, may be an isooleic acid or mixture of isomers of oleic acid, known to be formed by the action of zinc chloride on oleic acid. (3) The difference between the neutral equivalent and the saponification equivalent is probably due to the formation of acid anhydrides in the reaction, since no acetyl

number could be found for the acids of fractions two and three in this last distillation.

To further clear up the nature of these solid acids, they were carried through a lead salt-ether separation, as modified by Cocks and Christian (8) to separate solid iso-oleic acids from liquid acids. Thirty five grams of acids from a similar experiment, boiling range .55-215/0.3, neutral equivalent 537, and iodine number 59.2, were separated into a solid fraction and a liquid fraction. The solid fraction consisted of 54.4 percent of the whole. From the iodine number, it would appear to consist of iso-oleic acids and stearic acid. The whole acid might be considered as 39.4 percent of iso-oleic acids, 15.1 percent stearic acid, and 45.6 percent of unchanged oleic acid.

To find out if this solid unsaturated acid was the 10-, 11-oleic acid reported by Bauer and Panagoulas from the reaction of zinc chloride and oleic acid (3), the acid was oxidized to the glycol and split with periodic acid to locate the double bond. The entire sixteen grams of solid acids from the lead salt separation were dissolved in 46 cc of glacial acetic acid. Thirteen cc of 30% hydrogen peroxide were added and the mixture heated to 90°C, then allowed to stand overnight. The next morning the semisolid mass was washed with hot water, then taken up in ether. The ether solution was washed till neutral, then dried and the ether removed. An iodine number on the product showed 2.70 units. This corresponds to a 90% conversion into the glycol. To make sure that

the hydroxyl groups were not acylated, the material was given an alkaline hydrolysis before proceeding to the oxidation of the glycol.

To oxidize the glycol, the procedure of King (21) was used. Eighteen grams of the glycol were dissolved in 300 cc of 95% ethanol and heated to 40°C. To this was added a solution of 12 grams of potassium periodate dissolved in 600 cc of one normal sulfuric acid and cooled to 20°C. The solutions were mixed, allowed to react for ten minutes, and then cooled to 20°C, diluted with twice the volume of water and extracted with ether three times. The ether extracts were evaporated to dryness and gave an oil. The oil was steam distilled and the distillate extracted with ether. After washing with weak alkali, the ether extracts gave three grams of an aldehyde. Carbon and Hydrogen determinations on the aldehyde showed: Carbon, 71.5%, Hydrogen 12.21%. To see if a derivative could be prepared, the 2,4-dinitrophenylhydrazide was prepared according to the directions of Strain (30). The phenylhydrazide seemed to be a mixture of several isomers, since repeated recrystallizations would not raise the melting point above 60°C. Thus it seems that the solid isoöleic acids produced by the benzylation side reaction are not the 10,11-oleic acid alone.

Because of the low yield of benzylated acids in the previous experiment, another preparation was undertaken, using stannic chloride as the condensing agent. One mole of oleic acid, two moles of benzyl chloride, and five grams of stannic

chloride were heated at 150°C for five hours. At the end of this time the evolution of hydrogen chloride was practically at an end. After hydrolyzing and drying, the crude oil weighed 443 grams and contained 1.70 percent chlorine. This was removed by dimethylaniline, and the product vacuum distilled.

#### Distillation 4

Fractionation of 377 grams of  $\text{SnCl}_4$  benzylation product.

Frac	Boiling range.	wt. Frac.	% Frac.	N. E.	$I_2$	No.
I	135-170/0.1	17	4.4	332	---	---
II	170-220/0.1	98	25.3	320	---	---
III	220-250/0.1	20	5.2	314	---	---
IV	250-330/0.1	55	14.2	502	35.6	
Residue.		187	48.4	---	---	

These yields are seen to correspond closely to those of the previous experiment using zinc chloride. So, fraction II of distillation 2 and fraction IV of distillation 4 were combined and given a vacuum distillation.

#### Distillation 5

Refractionation of benzylation fractions, total 67 grams.

Frac.	Boiling range	wt Frac.	% Frac.	N. E.	$I_2$	No.
I	140-215/0.1	15	22.4	336	---	---
II	215-245/0.1	23	34.5	452	25.9	
III	245-300/0.1	18	26.9	557	23.2	
Residue		9	13.4	---	---	

The second fraction is close to the theoretical value for dibenzylsuccinic acid in neutral equivalent (462.39). So, the refractive index,  $n_{\text{D}}^{20}$ , was measured and found to be 1.5178

and the specific gravity,  $D_{\frac{20^{\circ}\text{C}}{40^{\circ}\text{C}}}$ , was found to be 0.98226. These values were used to calculate the molecular refractivities:

For dibenzyloleic acid (theory) 143.8

For dibenzylstearic acid(theo.) 144.3

From experimental values: 142.6

Carbon and hydrogen determinations showed:

Calculated for dibenzyloleic acid, carbon 83.1%, hydrogen 9.95%

Calculated for dibenzylstearic, carbon 82.8%, hydrogen 10.35%

Average of analytical values, carbon 82.2%, hydrogen 10.37%

The theoretical iodine number for dibenzyloleic acid is 55.0. As the iodine number obtained is only half of this, the product is evidently a mixture of dibenzyloleic and dibenzylstearic acids.

Because of doubt as to the validity of basing work on the stannic chloride and zinc chloride condensations products together, the preparation of dibenzyloleic acid was undertaken, using two moles of oleic acid, four moles of benzyl chloride, and ten moles of zinc chloride. After the usual treatment to remove the catalyst and combined chlorine, the product was distilled three times to give 52 grams of a fraction of nearly pure benzyloleic acids. This was fractionated once more:

#### Distillation 6

Final purification of dibenzyloleic acid.

Frac.	Boiling range	Wt. Frac. %	Frac. N. E. I <sub>2</sub>	No.
I	200-218/0.1	9	17.3	---
II	218-230/0.1	27	52.0	456 21.8
III	230-250/0.1	19	36.5	535 25.4
Residue		2	3.9	---

Combustions for carbon and hydrogen showed:

Fraction two-	carbon 82.2%, hydrogen 10.20% (average)
Fraction three-	carbon 83.1%, hydrogen 9.82% (average)
Dibenzylstearic	carbon 82.8%, hydrogen 10.35% (calc.)
Dibenzyloleic	carbon 83.1%, hydrogen 9.95% (calc.)

Fraction three lies closer to the values for dibenzyl-oleic acid than the second fraction, but this is probably due to the lowering of the carbon hydrogen ratio by anhydride formation, as its neutral equivalent is much higher than the theoretical. saponification equivalent shows that anhydrides are present.

The 27 grams of dibenzyloleic acid obtained from the last fractional distillation represent an overall yield of 2.9%, based on oleic acid. To improve the yield, a series of experiments at lower temperatures were conducted. Instead of 150°C, an aralkylation was carried out at 80°C in a thermostatically controlled bath. A reaction mixture containing two moles of benzyl chloride, one mole of oleic acid, and ten grams of stannic chloride had an initial iodine number of 47.3. At the end of 11 hours, the iodine number had fallen to 10.1, but the mixture was allowed to stand 10 days longer at room temperature before working up. In that time the iodine number fell to 6.1. The chlorine content (by Parr bomb) was found to be 5.75% after the excess benzyl chloride was removed by steam distillation. An attempt was made to distill a portion of this without removing the chlorine. 100 grams were taken and no attempt was made to trap the hydrogen chloride before

it passed through the vacuum pump.

#### Distillation 7

Fractionation of Chlorine containing benzylation product.

Frac.	Boiling range.	wt. Frac.	% Frac.	N. E. I <sub>2</sub>	No. % Cl
I	110-210/6.0 *	12	12	319	35.3 3.49
II	210-225/1.0	40	40	304	62.0 2.44
III	225-310/1.0	21	21	398	47.8 0.02
Residue		24	24	---	--- 0.00

\*(The hydrogen chloride evolved lowered the vacuum to 6.0 millimeters of Hg at one time, and corroded the pump slides so that they jammed after the distillation, and necessitated a thorough cleaning of the pump.)

Chlorostearic acid has a neutral equivalent of 318.7 and a chlorine content of 11.05%. The first fraction has a neutral equivalent of 319 but a chlorine content of only 3.49%. The high iodine number however shows that a large amount of oleic acid is present in the fraction. Hydrogen chloride has been shown to add to olefins in the presence of stannic chloride. (9) The next fraction has an even lower chlorine content, and contains more oleic acid and less chlorine. The third fraction contains the benzylation oleic and stearic acids. As the temperature of the distillate rises, the chlorine content decreases.

The remainder of the chlorine containing reaction product was treated with dimethylaniline to remove the chlorine, and then vacuum distilled. In this way a comparison may be made between the composition of the corresponding fractions resulting from the two distillations.

## Distillation 8.

Fractionation of 203 grams of chlorine free product.

Frac.	Boiling range.	wt. Frac.	% Frac	N. E.	I <sub>2</sub> No.
I	168-200/0.5	22	11.5	303	41.0
II	200-225/1.0	70	35.5	316	41.9
III	225-310/1.2	50	26.0	414	48.9
Residue.		50	26.0	---	---

In this distillation the neutral equivalent rises steadily with the boiling point, while the iodine number is nearly constant. The sum of both fractions number three, from this and the previous distillation, is 71 grams, or 15.4% of an impure benzylated fraction.

Because of the increased yield of distillable product at 80°C, another experiment using the same amounts of reactants was carried out in a thermostat held at 50°C. After 101 hours, the iodine number had fallen from the initial 47.3 to 9.2 units. The catalyst was removed by washing, and a steam distillation removed the unreacted benzyl chloride. The resulting product had the following analysis: Neutral equivalent 415, chlorine content 6.45%. This mixture was refluxed with dimethylaniline in excess to remove the chlorine, the reagent removed, and iodine number determined on the mixture.

## Distillation 9

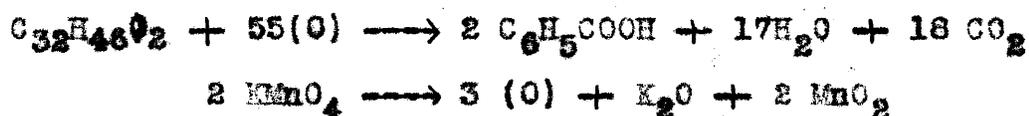
Fractionation of 219 grams of product, iodine number 28.4

Frac	Boiling range	wt. Frac.	% Frac.	N. E.	I <sub>2</sub> No.
I	110-185/1.0	56	25.5	307	46.5
II	185-235/2.0	30	13.7	327	41.0
III	235-310/1.0	77	35.0	409	35.9
Residue		45	20.5	2020	23.2

This distillation result shows that a still further rise has taken place in the percentage of benzylated acids. The yields of benzylation experiments are grouped together in table IV, page 28.

Oxidation of dibenzyloleic acid.

This was carried out with alkaline permanganate, using twice the stoichiometric porportion of oxidant based on the equations:



Nine grams, 0.0195 mole of dibenzyloleic acid, N E 456 from distillation 6, 1.1 gram of potassium hydroxide, and 226 grams of potassium permanganate were used. The permanganate was added as a saturated solution in water to the boiling solution of the acid and potassium hydroxide. The product was isolated in the usual manner, and recrystallized several times from water. The acid melted at 121°C and a mixed melting point with benzoic acid gave 119°C. Oxidations with dichromate and acid were less successful, as a tarry mass formed which did not yield any benzoic acid on working up by the usual methods. Oxidations in sealed tubes with 1.20 specific gravity nitric acid were also unsuccessful, as the long oleic acid chain which was oxidized off formed so large a porportion of the charge that the evolved gases usually blew up the tube before the oxidation was complete. As only 0.5 gram of acid was used in each tube, which had a volume of about 25 cc, it is seen that the yield of each oxidation was difficult to purify in such small amounts.

TABLE IV  
 Yields of Benzylated Product.  
 Effect of variables.

Ration of BzCl to oleic acid	Catalyst *	Temperature (°C)	Boiling range (°C/mm)	Yield, %.
1:1	ZnCl <sub>2</sub>	150	280-310/0.5	11.0
2:1	ZnCl <sub>2</sub>	150	250-340/0.1	13.1
2:1	SnCl <sub>4</sub>	150	220-330/0.1	19.4
2:1	ZnCl <sub>2</sub>	80	225-310/0.1	21.0
2:1	ZnCl <sub>2</sub>	80	225-310/1.2	26.0
2:1	ZnCl <sub>2</sub>	50	235-310/1.0	35.0

\* In all of these experiments five grams of the catalyst was used per mole of oleic acid.

## THE ALKYLATION OF OLEIC ACID

A preliminary experiment showed that catalytic amounts of aluminum chloride were not enough to induce the desired reaction. When 0.4 mole of aluminum chloride was used per mole of methyl oleate, one mole of butyl chloride was recovered unreacted, and the iodine number of the oleate was unchanged. Because of the known molecular complexes formed by aluminum chloride and the carbonyl group (29) the ratio of aluminum chloride was raised to 1.20 moles per mole of oleic acid, and an experiment was carried out using one mole of oleic acid, 1.20 moles of aluminum chloride, one mole of n-butyl chloride, and five moles of orthodichlorobenzene was added as an inert solvent. Orthodichlorobenzene was selected as a solvent because it had previously been employed in a similar capacity (16) and had been found to be inert. Here however, it was found that the solvent reacted with the butyl chloride and the oleic acid, although the conditions of the experiments produced no appreciable alkylation of the oleic acid.

The reaction was carried out at 0-10°C, adding the oleic acid and halide to the aluminum chloride suspended in orthodichlorobenzene; and torrents of hydrogen chloride gas were given off. The mixture was hydrolyzed, using 500 cc of concentrated hydrochloric acid and ice, and the reaction mass was washed free of aluminum chloride and acid. The orthodichlorobenzene solvent was removed by steam distillation. A

dark oily product remained which was distilled in vacuo:

### Distillation 10

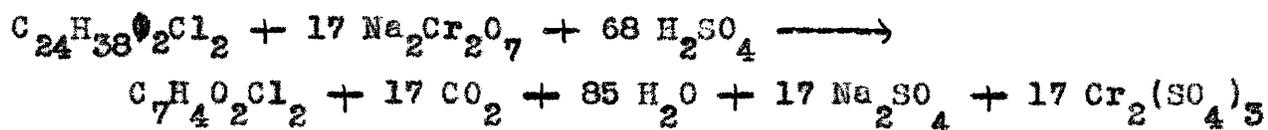
Fractionation of 248 grams of product from alkylation.

Frac.	Boiling range.	Wt Frac.	% Frac	N. E.	I <sub>2</sub> No.	% Cl.
I	60-130/0.2	9	3.6	528	---	---
II	130-215/0.1	50	20.2	297	6.41	---
III	215-260/0.2	83	33.4	365	15.9	10.28
Residue		100	40.3	---	---	---

Fraction three had a saponification equivalent of 361, almost the same as its neutralization equivalent of 365; an analysis for carbon and hydrogen showed: carbon 70.2%, hydrogen 9.90%. This carbon-hydrogen determination definitely indicated that an aromatic ring had been added to the oleic acid molecule. To get additional material, a duplicate of the experiment was run, and the corresponding vacuum distillation fractions were combined.

The combined fractions having the boiling range 215-260°C at 0.2 mm were given two vacuum distillations, and twenty percent of this material was found to distill in the range 223-224°C/0.1mm and had a neutral equivalent of 429. Chlorine determinations gave 15.80 and 15.83%, and the iodine number was less than one. A carbon and hydrogen determination gave the values: carbon 67.1%, hydrogen 8.80%. This material was clearly not the expected alkylchlorostearic acid.

For further structure proof, an oxidation with chromic acid was carried out. A 33 percent excess of oxidant was used over the quantity necessitated by the stoichiometric relations in the equation:



Ten grams of the fraction were oxidized following the general procedure given in Organic Syntheses (14) and a 10 percent yield of 3,4-dichlorobenzoic acid was obtained. This was proven by the mixed melting point with a known sample of 3,4-dichlorobenzoic acid. The known melted at 206.5-207.0°C, the oxidation acid melted at 205-6°C, and the mixed melting point was 206.5-207.0°C. The chlorine content of the acid checked with the theory for 3,4-dichlorobenzoic acid. A comparison of some of the analytical data for the unknown acid with the theoretical values for 3,4-dichlorophenylstearic acid shows that they are identical.

	Carbon,%	Hydrogen,%	N.E.	Chlorine,%	Molecular refrac.
Analytical:	67.1	8.80	429	15.84	122.527
Theoretical:	67.1	8.91	429.12	16.52	120.701

To discover the part that the n-butyl chloride took in the reaction, the steam distilled solvent was distilled carefully, with the following results:

#### Distillation 11

Refractionation of orthodichlorobenzene recovered solvent.

Fraction	Boiling range	wt fraction.	% fraction.
I	100-177/762mm	8	1.2
II	177-250/762	580	90.0
III	250-254/762	25	3.9
IV	254-280/762	33	5.1

Fraction three was subjected to a chromic acid oxidation;

ten grams of this fraction gave 0.2 gram of an acid whose neutral equivalent was 190.9. Theoretical for dichlorobenzoic acid is 190.9. A mixed melting point with a known sample showed a melting point of 205.8-206.5°C; known 3,4-dichlorobenzoic acid melted in the same test at 207.0-207.5°C. Only alkyl-dichlorobenzenes would give this acid on oxidation.

The low boiling fractions from the distillation of the oleic acid reaction product were semi-solid at room temperature, had a low iodine number, and a neutralization equivalent of 297. These are enough to suggest the presence of stearic acid. Accordingly the material was chilled in the refrigerator and poured into a cold Buchner funnel, and as much as possible of the oil filtered off by suction. 19 grams or 17% of the solid material remained on the filter paper. This was recrystallized twice from acetone, but analytical data showed that it apparently contained a material of lower molecular weight than stearic acid. The material was next carried through a lead salt-ether purification to remove any oleic acid, reconverted to the acid and analyzed again. Combustions gave the result:

Carbon 75.5%, Hydrogen 12.60% av. for purified acid, while Carbon 75.9%, Hydrogen 12.75% are the values for stearic acid. Calculating from the iodine number, more than ninety percent of the low boiling fatty acid fraction is stearic acid. The hydrogen probably comes from the reaction mentioned by the Indian researchers headed by Chowdhury (7), as polymerization reactions gave an undistillable residue of 40.3 percent of

the reaction product.

The above work has shown that there was no appreciable alkylation of oleic acid. All the butyl chloride used in the reaction reacted with the orthodichlorobenzene solvent, as none was found in the steam distilled solvent. Tertiary butyl chloride was used in another attempted alkylation, but the only significant difference was a smaller yield of 3,4-dichlorophenylstearic acid.

#### THE ACYLATION OF OLEIC ACID

Because the acylation of aromatic hydrocarbons demands molecular proportions of aluminum chloride, 1.30 moles of aluminum chloride were used for each mole of ethyl oleate in a preliminary experiment. 113 grams, 0.365 mole, of ethyl oleate and 349 grams, 2.84 moles, of nitrobenzene solvent were mixed and cooled to 0°C. 63 grams of aluminum chloride, 0.475 mole, were added all at once to the mixture. The solution turned dark red, showing complex formation, but no gas was evolved. 29 grams, 0.365 mole, of acetyl chloride were added dropwise to the mixture. Hydrogen chloride was evolved during this addition. After standing overnight, the mixture was hydrolyzed with 100 cc of concentrated hydrochloric acid and about a kilogram of ice. The nitrobenzene solution was washed free of acid and the nitrobenzene removed by steam distillation, 89.5 percent being recovered. The remaining oil was dried and then subjected to a vacuum distillation to isolate the hypothetical ethyl acetylchlorostearate from any unchanged ethyl oleate. However no hydrogen chloride was evolved during the distillation:

## Distillation 12

Fractionation of 68 grams of acylated ethyl oleate.

Frac.	Boiling range	wt. Frac.	% Frac.	Sap. Equiv.	I <sub>2</sub> No.
I	158-185/0.2	30	44.0	309.8	18.1
II	185-240/0.2	5	7.4	298.5	---
III	240-310/1.0	6	8.8	281.	---
Residue.		21	31.0	289.	---

The saponification equivalent of the original ester was 308.3, and its iodine number was 83.5. The theoretical values are 310.23 and 82.0 respectively. It is shown that the reaction has produced little change in the saponification equivalents, although the iodine number of the semi-solid first fraction is lower than that of the original material. This is probably due to hydrogenation, since much of the ester has been polymerized to an undistillable resin.

It is possible that alkyl acetyloleates might split off the added group during the distillation. Nenitzescu and Ciocanescu (27) found that reactions using aluminum chloride in cyclohexane solvent resulted in hydrogenated products, because of the side reactions of the solvent and aluminum chloride.

For example,  $2 \text{C}_6\text{H}_{12} \rightarrow \text{C}_6\text{H}_{11}-\text{C}_6\text{H}_{11} + \text{H}_2$

One mole of oleic acid, one mole of acetyl chloride, and five moles of cyclohexane were mixed and three moles of aluminum chloride were added in small portions, keeping the temperature between zero and ten degrees Centigrade. The mixture was warmed gradually to 70°C and held there four hours. After hydrolysis with ice and concentrated hydrochloric acid, the cyclohexane solvent was removed by distillation with steam

and the remaining oil was dried with anhydrous  $\text{CaSO}_4$ .

### Distillation 13

Fractionation of 263 grams of acylated oleic acid.

Frac.	Boiling range.	Wt. Frac.	% Frac.	N. E.	$\text{I}_2$ No.
I	130-205/0.5	38	14.5	737	60.8
II	205-250/0.5	43	16.4	451	52.2
III	250-315/1.0	18	6.8	626	58.8
Residue.		155	58.9	---	---

As might be expected, the high molecular ration of aluminum chloride to oleic acid produced many side reactions involving the oleic acid, as shown by the high neutralization equivalents. Hydrogenation in cyclohexane solution does not seem to have occurred, judging from the high iodine numbers of the distillation fractions. Some hydrogen chloride did evolve during the distillation, however.

An experiment using no solvent followed. One mole of methyl oleate and one mole of acetyl chloride were mixed in a flask and cooled to  $10^\circ\text{C}$ . Then 1.2 gram moles of aluminum chloride were added gradually. Only a small amount of hydrogen chloride was evolved during this addition. The flask and contents were now heated to  $70^\circ\text{C}$  and held there for four hours. During this heating, hydrogen chloride was given off in large amounts. The mixture was hydrolyzed using ice and water only. After washing acid free and drying, the product was distilled. The original methyl oleate was prepared by esterifying U. S. P. oleic acid with methyl alcohol, neutralizing the free acid, and distilling the residual methyl oleate after washing out the soap with large volumes of water. It had a saponification

equivalent of 296 and an iodine number of 35.8

#### Distillation 14

Fractionation of acylated methyl oleate.

Frac.	Boiling range	Wt. Frac.	% Frac.	Sap. Equiv.	I <sub>2</sub> No.
I	130-190/0.1	94	30.4	309	38.3
II	190-197/1.5	62	20.0	331	46.4
III	197-220/2.0	17	5.5	331	---
Residue.		125	40.4	331	---

The first fraction is probably partially hydrogenated methyl oleate. Fraction two, analyzed for chlorine, showed 6.55 percent. A combustion gave: carbon, 70.0%, hydrogen 10.81%. If this fraction contained methyl acetylchlorostearate, 69.3%, and methyl oleate, 30.7%, the resulting mixture would analyze nearly the same as the values found. The iodine number would be lower by 19 units however. Because hydrogen chloride splits out during the distillation, it is probable that purification of this compound cannot be effected by distillation methods, since increasing amounts of methyl acetyl-oleate would be formed in each successive distillation.

The reagents introduced by Girard and Sandulesco (15) for the separation of ketones offered a possible solution to this problem. Reagent "P", pyridiniumaceto-hydrazone hydrochloride, was synthesized and applied to the reaction product of oleic acid and propionyl chloride. Propionyl chloride was used because the increased molecular weight of the addition compound compared to that of oleic acid should produce a greater differentiation of physical properties. Stannic chloride was used as the catalyst in this new preparation because

of its milder action compared to aluminum chloride, and the fact that Colonge and Mostafi (9) found stannic chloride to be the best catalyst for the acylation of olefins. They obtained yields of 60 percent in the reaction of trimethylethylene and propionyl chloride, compared with 13 percent for aluminum chloride.

One mole of propionyl chloride and one mole of oleic acid were mixed together with a high speed stirrer, and after 33 minutes of stirring, five grams of stannic chloride were added. The iodine number of the mixture fell slowly from 67.1 (no addition) to 38.7, after standing 68 hours at room temperature. This should indicate the presence of 42.3 percent of the addition compound. The mixture was washed several times with hot water and dried with sodium sulfate. 281 grams of a dark colored oil were obtained.

250 grams of this oil were treated with dimethylaniline to remove hydrogen chloride. After this process 237 grams of chlorine free oil remained.

#### Distillation 15

Fractionation of dehydrohalogenated addition product.

Frac.	Boiling range	Wt. Frac.	% Frac.	N. E.	I <sub>2</sub> No.
I	160-170/0.1	53	23.3	300	66.1
II	170-190/0.1	55	24.2	306	75.9
III	190-230/0.1	33	14.5	393	56.5
IV	230-280/0.1	6	6.4	430	48.1
Residue		68	29.9	---	----

The expected propionyleoleic acid should have a neutral

equivalent of 338 and an iodine number of 75.1. No fraction approached this in composition.

Girard's reagent "P" was now applied to the chlorine containing addition product, the dehydrohalogenated oil, and distillation fractions I, II, and III. Five grams of the material was weighed out and refluxed with a solution of two grams of the reagent dissolved in 90 cc of absolute ethanol and 10 cc of glacial acetic acid. This amount of the reagent was a 100 percent excess over the amount necessary to extract 0.845 grams of ketone. After refluxing one hour, each solution was poured into one liter of cold water containing 8 grams of sodium carbonate, which adjusts the pH so that the water soluble hydrazide of the ketoacid is not hydrolyzed. Successive extractions with ether removed all matter which was not water soluble. The solution was then made strongly acid with 27 cc of concentrated sulfuric acid, and after standing one hour to insure complete hydrolysis of the hydrazide, another series of ether extractions were made to extract the ketonic material. No more than a few milligrams were obtained in each case.

Girard's reagent "T", trimethylammoniumacethydrazide hydrochloride, gives hydrazides which are more soluble than those of the "P" reagent. If the failure to extract ketones from the reaction mixture was due to insufficient solubility of the hydrazide, reagent "T" might prove effective. However, a series of assays with reagent "T" were no more effective than the other ketone reagent.

These ketoöleic and ketostearic acids of course have a

free carboxyl group. It is possible that this is the cause of the failure of the Girard reagents to extract any ketones from the reaction products. An extraction of the chlorine containing addition product was carried out using anhydrous ethylene glycol instead of water and sodium carbonate to dissolve the ketone hydrazone. The alcohol used as the first solvent was removed under vacuum and the resulting glycol solution was extracted with ether as before, and then acidified to break up the hydrazone. Still no ketone was obtained. This experiment definitely ruled out the possibility of the ketone hydrazone having been hydrolyzed during the first ether extraction.

To eliminate the effect of the carboxyl group, a series of experiments were now carried out on methyl oleate which was prepared from the U. S. P. oleic acid. One mole of methyl oleate and one mole of acetyl chloride were mixed and then ten grams of stannic chloride were added. After two and one half hours, the catalyst was washed out and the oily product was dried. The iodine number of the ester was now 44.5, indicating 55 percent addition of the chloride.

Hilditch (18) has given the details of a method useful in separating unsaturated fatty acids from saturated acids. As methyl acetylchlorostearate is saturated, and methyl oleate is unsaturated, it may be applied here. Thirty grams of the reaction product of methyl oleate and acetyl chloride were dissolved in 500 cc of acetone and placed in the flask of a Soxhlet extraction apparatus. One hundred and twenty grams of potassium permanganate were placed on top of a

layer of glass wool in the compartment which ordinarily houses the extraction thimble. When refluxed, the condensing acetone is saturated with permanganate and pours down into the lower flask to react with the methyl oleate, forming pelargonic acid and the half ester of azelaic acid. After all the permanganate had been dissolved, the acetone was distilled off, and the manganese dioxide residue was dissolved by adding a liter of water and passing in sulfur dioxide gas. The entire mixture was extracted with petroleum ether and the water solution was discarded. Three successive extractions with 100 cc of a ten percent solution of potassium hydroxide dissolved in fifty percent aqueous alcohol removed all acid products. The petroleum ether was washed alkali free and dried. Evaporation of the ether in vacuo left a residue of 11.5 grams of an oil having an iodine number of 6.2 This corresponds to a methyl oleate content of 13.9 percent, so the oxidation was repeated. This time the residue was 10.5 grams with an iodine number of 1.00 Analysis of this product is compared with that of the expected methyl acetylchlorostearate:

	Carbon, %	Hydrogen, %	Chlorine, %	I <sub>2</sub> No.
Found:	66.25	11.25	7.30	1.00
Theory:	67.3	10.49	9.47	0

These figures suggest that other saturated materials in the methyl oleate are not removed by the oxidation procedure, so to remove these, this oxidation product was reacted with reagent "T" and purified from non ketonic material. The new analysis of this product now was:

	Carbon, %	Hydrogen, %	Chlorine, %	Molec. Refrac.
Found:	67.3	10.30	9.45	105.3
Theory:	67.3	10.49	9.47	105.6

The molecular refraction was calculated from the measured index of refraction,  $n_{\text{Abbe}}^{20^{\circ}\text{C}} = 1.4665$ , and the density,  $D_{4^{\circ}\text{C}}^{20^{\circ}\text{C}} = 0.9830$

These results indicate the identity of the purified compound as methyl acetylchlorostearate. Proof of the presence of the ketone group is also furnished by the circumstance of the purification by means of Girard's reagent. The yield of the oxidations was 10.5 grams. If it is assumed that all the methyl stearate and unsaponifiable material present in the oleate were not removed by the oxidation, then in the thirty grams of material taken for analysis 2.1 grams of this matter persisted through the oxidation. This checks with the chlorine determination, which indicated 77.1 percent of methyl acetylchlorostearate in the product of the oxidations. A yield of 28 percent of methyl acetylchlorostearate (calculated on the basis of the oleate used) was obtained in the oxidations. This is 80 percent of the yield indicated by the iodine number of the ester after the acylation reaction.

To check on the extraction of methyl acetylchlorostearate from the primary reaction product after the stannic chloride has been washed out, 120 grams of this were refluxed with a solution of 30 grams of Girard's reagent "T" dissolved in 270 cc of absolute alcohol plus 30 cc of glacial acetic acid. After cooling, this solution was poured into a solution of 24 grams of sodium carbonate dissolved in a liter and a half

of water. Four ether washings removed 106 grams of oil. A dark intermediate layer lay on top of the water layer. This was separated and found to be entirely soluble in water when shaken with a liter of water. Acid was then added to both water solutions, and the ketone was extracted with ether after an hour had been allowed to complete the hydrolysis. The ether solutions were dried with sodium sulfate and the ether removed in vacuo. The solution of the dark intermediate layer gave 12 grams of an oil which had the same refractive index,  $n_{\text{Abbe}}^{20^{\circ}\text{C}} = 1.4790$ , as the two grams of oil obtained from the lower water layer. The two portions were combined and analyzed: Carbon, 70.8 percent, hydrogen, 10.03 percent, chlorine, 4.98 percent, iodine number, 56.8 units.

These values can only be rationalized if the ketone fraction consists of 52.8 percent of the saturated methyl acetylchlorostearate and the remainder is methyl acetyloleate. The analysis checks perfectly for this figure. The conclusion then is that Girard's reagent may be used to extract the ketone fraction if the carboxyl group of oleic acid has been esterified. In this case the yield was only one third of the yield calculated from the iodine number. Longer refluxing of the reagent would probably increase this figure.

Improvement of the yields of addition product may be effected by the use of larger amounts of stannic chloride catalyst. A table of the iodine numbers attained by various experiments is appended. (Table V)

TABLE V

## IODINE NUMBERS OF ACYLATION EXPERIMENTS.

Components	Catalyst	Time	Temperature	I <sub>2</sub> No.	Calc. Addn., %
Oleic acid- Acetyl chloride	SnCl <sub>4</sub> **	1 hr.	-10°C	21.9	9.0
Oleic acid- Propionyl chloride	"	15 min.	27°C	60.8	9.1
same	"	1 hr.	"	58.0	14.
same	"	19 hrs.	"	35.0	49.
Oleic acid- Acetyl chloride	SnCl <sub>4</sub>	300 hrs.	30°C	28.1	61.
Methyl oleate- Acetyl chloride	SnCl <sub>4</sub>	2½ hrs.	30°C	44.5	35

\*\* Ten grams of catalyst per mole of oleic acid or oleate.

The next figure is for 20 grams of SnCl<sub>4</sub>/mole:

Methyl oleate- Acetyl chloride	SnCl <sub>4</sub>	17 hrs.	30°C	28.5	58.
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Thirty grams of SnCl<sub>4</sub> were used in this experiment:

Methyl oleate- Acetyl chloride.	SnCl <sub>4</sub>	17 hrs	50°C	26.6	61.
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(Experiments in which large amounts of stannic chloride were used also showed a considerable evolution of heat. The temperature rose to 55°C, where acetyl chloride boils, but no chloride was lost from the mixture. Some dehydrochlorination may have taken place but less than a gram was lost from a mole)

## V SUMMARY

An activity series has been determined for the reaction of oleic acid and various halides in the presence of stannic chloride. Calculations of the amount of addition product formed are shown to be in error when the reaction is carried out at high temperatures. Dibenzyloleic acid was isolated in small yield from the reaction of benzyl chloride and oleic acid in the presence of zinc chloride. Isooleic acids and a modified benzyl resin were the main products of this reaction. N-butyl chloride and oleic acid in the presence of aluminum chloride and in orthodichlorobenzene solvent give 3,4-dichlorophenylstearic acid, butylated orthodichlorobenzene, and stearic acid. The addition product of acetyl chloride and oleic acid cannot be isolated by ordinary means, but methyl acetylchlorostearate is readily obtainable from methyl oleate, acetyl chloride and a stannic chloride catalyst.

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### Abstract

THE ARALKYLATION, ALKYLATION AND ACYLATION OF OLEIC ACID.

#### Biography of the Author and Publications.

Born Sept. 27, 1909 in Lima Ohio. Graduated from Missoula County High School, Missoula, Montana, 1927. B. A. in Chem. from University of Montana, 1931. M. Sc from University of Ill. at Urbane, Ill., 1932.

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#### Publications:

"Arylstearic Acids from Oleic Acid" L. J. Stirton and R. F. Peterson, Ind. Eng. Chem. 31 866 (1939)

"Sulfoarylstearic acids, wetting properties of the sodium salts" L. J. Stirton, R. F. Peterson and R. E. Groggins, Ind. Eng. Chem. August 1940

(An application for a patent has been made in the above three names as the result of this work)

Abstract of a thesis submitted to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

THE ARALKYLATION, ALKYLATION AND ACYLATION OF OLEIC ACID.

This work is part of a systematic investigation of the possibilities of producing useful products by the chemical treatment of fats and oils. In the presence of a metal chloride catalyst and using alkyl or acid chloride reagents, alkylation or acylation takes place at the double bond of oleic acid or of methyl oleate. From benzyl chloride, zinc chloride and oleic acid, a dibenzyloleic acid was isolated in small yields. The principal products were an isomerized oleic acid and a benzyl resin. From normal or from tertiary butyl chloride, aluminum chloride and oleic acid, in orthodichlorobenzene solvent, no butylated fatty acid could be obtained. Instead the products were butyl-3,4-dichlorobenzene, 3,4-dichlorophenylstearic acid, stearic acid, and a residue remaining after distillation in vacuo.

In contrast to the benzylation and butylation experiments the acylation of methyl oleate with acetyl chloride was easily effected. Methyl acetylchlorostearate could be isolated in an impure state, or more satisfactorily by a method involving the oxidation and removal of unsaturated material, followed by an extraction with Girard's reagent to isolate the ketonic ester in a yield of about thirty five percent. The methyl acetylchlorostearate is probably a mixture of

the isomers methyl 9-acetyl-10-chlorostearate and methyl  
9-chloro-10-acetylstearate.

**Thesis of Robert Frederick Peterson approved**

**Date** \_\_\_\_\_ **Professor in charge of thesis** \_\_\_\_\_