Abstract

AMYLSTEARIC ACIDS

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Preparation of 2-Aminoanthraquinone from Phthalic Anhydride and Bromobenzene. --P. H. Groggins, A. J. Stirton, and H. F. Newton--Ind. Eng. Chem. 23 893 (1931).

Amination by Ammonolysis I. Properties and Reactions of Aqueous Ammonia System II. Effect of Catalysts in Ammonolysis III. Effect of Inorganic Salts--P. H. Groggins and A. J. Stirton--Ind. Eng. Chem. 25 42,169,274 (1933).

Condensation of Carboxylic Acids--P. H. Groggins, R. H. Nagel, and A. J. Stirton--Ind. Eng. Chem. 26 1313 (1934).

Chapter VI. Amination by Ammonolysis--P. H. Groggins and A. J. Stirton--"Unit Processes in Organic Synthesis"--McGraw-Hill Book Company, Inc. (1935).

Amination by Ammonolysis. Effect of Ammonia Concentration--P. H. Groggins and A. J. Stirton--Ind. Eng. Chem. 28 1061 (1936).

Recent Progress in Amination by Ammonolysis--P. H. Groggins and A. J. Stirton--Ind. Eng. Chem. 29 1353 (1937).

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.

ARYLSTEARIC ACIDS

Five new arylstearic acids, p-methoxyphenylstearic, p-tolylstearic, p-chlorophenylstearic, p-bromophenylstearic and p-xenylstearic have been prepared from oleic acid and the appropriate aromatic compound in the presence of aluminum chloride. Ethyl oleate behaves similarly in such a reaction. The acids in all cases are viscous oils after isolation under reduced pressure, probably because they represent a mixture of the 9- and 10-arylstearic acids. Partial proof of structure has been obtained by oxidation to the simple substituted aromatic acid and by values of molecular refractivities. The acids form solid derivatives with S-benzylthiuronium chloride. The arylstearic acids may find uses (1) as an addition agent to lubricants (2) as soaps by conversion to salts of triethanolamine or related bases (3) as wetting agents by conversion to a sulfonated derivative (4) as synthetic waxes by conversion to high molecular weight esters.

Thesis of Alexander J. Stirton approved

Date_____ _____
Professor in charge of thesis

A R Y L S T E A R I C A C I D S

By

Alexander J. Stirton

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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I. INTRODUCTION

It was the purpose of this investigation to study the preparation of new arylstearic acids from oleic acid and an aromatic compound by the Friedel and Crafts reaction. Such compounds have a possible utilization (1) as addition agents to lubricants, (2) as soaps by conversion to salts of triethanolamine or related bases, (3) as wetting agents by conversion to a sulfonated derivative (4) as synthetic waxes by conversion to high molecular weight esters. The conversion of these arylstearic acids into such soaps, wetting agents, or waxes, has not here been studied, but is contemplated for the future. The present investigation deals with the preparation of p-tolylstearic, p-chlorophenylstearic, p-bromophenylstearic, p-methoxyphenylstearic, and p-xenylstearic acids.

Phenylstearic acid was made by Nicolet and de Milt (37) from benzene and oleic acid in the presence of aluminum chloride. There is an indication this acid had been earlier prepared by Marcusson (30) by the same means in the course of an investigation of the polymerization of fatty oils by air and by chemicals. Since 1927 reference to this acid has appeared in connection with a study in the rate of phenylation of oleic acid (49), the properties of lubricating greases made from soaps of the acid (19), the establishment that phenylstearic acid prepared by the Friedel and Crafts reaction is a mixture of approximately equal proportions of 9- and 10-phenyloctadecanoic acids (24), claims for improvements in

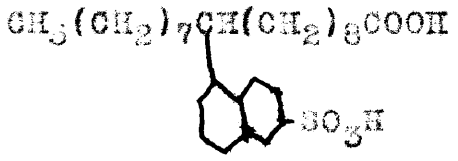
compounded lubricating oils (35,36,54) and improvements in the method of preparation (32) of phenylstearic acid.

Nicolet and de Milt (37) stated that "under conditions analogous to those used in the preparation of phenylstearic acid, oleic acid also reacts with toluene and naphthalene. In the latter case, carbon disulfide was used as solvent. The nature of the reaction appears to be the same in all these cases, but the products were not further studied." The preparation of xylystearic acid and of α-naphthylstearic acid has since been reported.

Xylystearic acid was made by Schmidt (49) from xylene, oleic acid, and aluminum chloride as an experiment paralleling his study of the rate of phenylation of oleic acid. The product after hydrolysis and removal of solvent was not further purified. It had an iodine number of 13, a neutralization equivalent of 389.6 (theoretical=388.4) and the silver salt analyzed 21.77% Ag (theoretical=22.02% Ag). The quality of the oleic acid used was not stated. Presumably it was a C.P. grade or better, otherwise impurities in the original oleic acid would remain in the final product, since this was not purified by distillation. The orientation of substituents in the benzene ring of xylylstearic acid was not established.

α-Naphthylstearic acid was prepared by Schlutius (48) from naphthalene, oleic acid and aluminum chloride. It was then sulfonated and found to be identical with Twitchell's reagent. On the basis of the oxidation products of the sulfonated naphthylstearic acid the Twitchell reagent is either

I, II, III or IV or is a mixture of two or more of these compounds:



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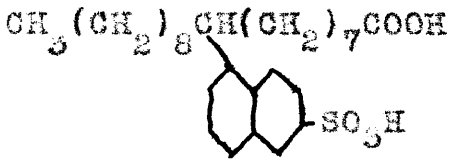

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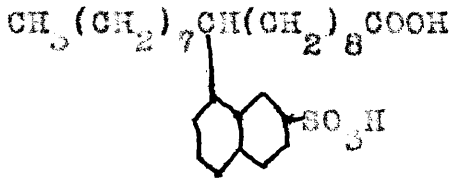

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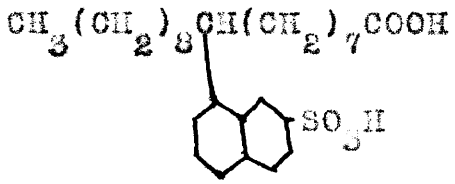
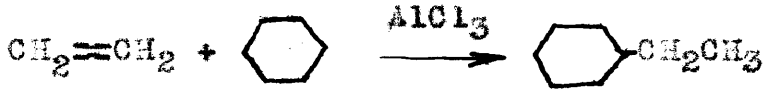


IV

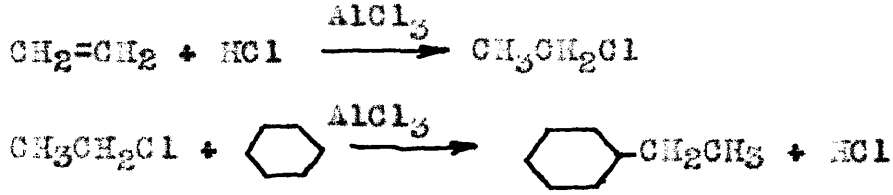
II. HISTORICAL

The reaction between an olefin and an aromatic compound, in the presence of aluminum chloride, to yield a saturated condensation product, by the apparent addition of an aryl radical at one of the doubly bound carbon atoms, and a hydrogen atom at the other, was known at an early stage in the history of the Friedel and Crafts reaction (3). The simplest case, and the earliest known is the reaction between ethylene and benzene to yield ethylbenzene.



Alkylations effected by such means apparently proceed through the intermediate formation or an alkyl chloride (3).

Hydrogen chloride is present as an impurity in the aluminum chloride, is produced by reaction of aluminum chloride with traces of moisture in the system, may be produced by a side-reaction between aluminum chloride and one of the reaction components, or is introduced deliberately by passing in dry hydrogen chloride. Theoretically only a trace would be sufficient, for it is regenerated on alkylation.



Alkylations by means of an olefin are similar to alkylations with alkyl halides in requiring only a catalytic quantity of aluminum chloride and in producing a mixture of mono- and polyalkylated benzenes. The factors involved in efficient alkylation have been studied by Reid and co-workers (5, 33, 34).

The cyclic olefins (6, 29) behave similar to ethylene and the reaction has been generalized to all substances having a double bond susceptible to reaction with an aromatic nucleus in the presence of aluminum chloride.

Arylfatty acids were made by Kykman (13, 14, 15, 16) from lactones, unsaturated acids, and halogenofatty acids by means of the Friedel and Crafts reaction. Benzene, toluene and ethylbenzene were the aromatic compounds employed, and he worked for the most part with acids containing from 3 to 5 carbon atoms. He began his study with γ-lactones, and prepared γ-methyl-γ-phenylbutyric acid, γ-methyl-γ-tolylbutyric acid, and γ,γ-diphenylbutyric acids:

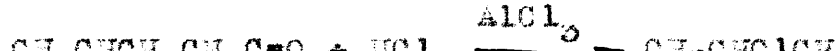
$$CH_3CHCH_2CH_2C{=}O + C_6H_6 \xrightarrow{AlCl_3} CH_3CH(C_6H_5)CH_2CH_2CO_2H$$

$$CH_3CHCH_2CH_2C{=}O + C_6H_5CH_3 \xrightarrow{AlCl_3} CH_3CH(C_6H_4CH_3)CH_2CH_2CO_2H$$

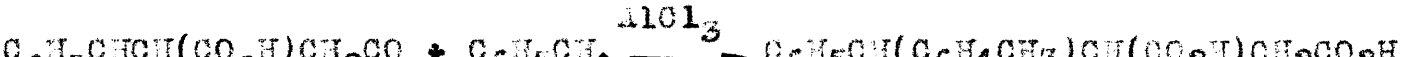
$$C_6H_5CHCH_2CH_2C{=}O + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_2CHCH_2CH_2CO_2H$$

At this time (13) he thought the reaction to proceed by

the mechanism:



In a following paper (14) he extended this reaction to paraconic acids.



He later found (15) that the presence of an α- or β-COOH or a γ-CN in a γ-lactone would frequently prevent a successful Friedel and Crafts reaction.

On continuing his investigations (15, 16) he used unsaturated acids and halogenofatty acids instead of lactones. A number of α- and β-monohalogenated fatty acids were found to be unreactive. The assumption that the addition of aromatic hydrocarbons to an unsaturated acid or lactone depends upon a preliminary formation of the hydrogen chloride addition product was not therefore considered a satisfactory explanation of the reaction.

Many of the simple and variously substituted crotonic, cinnamic and acrylic acids were found to yield an arylfatty acid with benzene and aluminum chloride. In some cases the product could not be made to crystallize, for instance β,γ-hydrosorbic acid, $CH_3CH_2CH{=}CHCH_2CO_2H$, gave a phenylated acid, probably a mixture of β- and γ-phenylhexanoic acid. Reactions with toluene did not always parallel reactions successful with benzene, for instance toluene and crotonic acid would not react, and the product from β-methylcrotonic acid and toluene was not crystallizable whereas the α-phenyl-β-methylcrotonic acid so produced from benzene melted at 58-59°.

The Friedel and Crafts reaction was first extended to the higher olefinic fatty acids by Marcusson in 1920. (30). This investigator had been concerned with the effect of chemical agents on the polymerization of fatty oils. Oleic acid when treated in benzene solution with aluminum chloride did not appear to polymerize, but instead, judged from neutralization equivalent, cryoscopic determination of the molecular weight, and the very low iodine number, the viscous oil formed was phenylstearic acid. Elaidic, erucic, linoleic and clupanodonic acids were stated to behave in a similar manner, and a reaction mechanism was suggested. The reaction was believed to be of general applicability to benzene homologs such as toluene and xylene, as well as naphthalene, anthracene, nitrobenzene, anisole, phenetole, etc.

The experiments of Marcusson were incomplete in proving

the constitution of the phenylstearic acid he prepared and his product was rather impure (neutralization equivalent, found--335; theoretical--360). His results were in general indicative rather than conclusive for he was primarily interested in the polymerization of fatty oils.

Phenylstearic acid was definitively prepared by Nicolet and de Milt (37). The phenylstearic acid, prepared from benzene and oleic acid, in the presence of aluminum chloride, was isolated after fractionation under reduced pressure as a clear, viscous oil which could not be made to crystallize. Numerous attempts at preparing a crystalline derivative were unsuccessful, for in all cases the products, although giving satisfactory analyses, were likewise oils. The salts of phenylstearic acid were the only solids obtained and none of these were found suitable for recrystallization. It was considered most likely the product, prepared in 35% yield, was 10-phenylstearic acid, but the position of the phenyl group could not be proven. Phenylstearic acid was very resistant to oxidation with hot alkaline permanganate; benzoic acid was the only product isolated. The authors note "Oleic acid is by far the most complex olefin to which the reaction with benzene and aluminum chloride has been applied."

Later references to phenylstearic acid (49,19, 24, 35, 36, 54, 32) to xylylstearic acid (49) and to naphthylstearic acid (48) have been noted in the INTRODUCTION.

Several phenyl substituted aliphatic acids were prepared by Harmon and Marvel (24) for the purpose of making them available for tests of Knoop's theory of β-oxidation. A method other than the Friedel and Crafts reaction was used and both 9- and 10-phenyloctadecanoic acids were made, as well as the corresponding p-bromophenacyl esters. The p-bromophenacyl ester of the phenylstearic acid from oleic acid, benzene and aluminum chloride was also prepared. Comparing the melting-points of the three esters, it was judged that the product from the Friedel and Crafts reaction was a mixture containing about equal amounts of the two isomers.

It has been found that esters of olefinic higher fatty acids can be used as well as the acids themselves in the Friedel and Crafts reaction.

Fourneau and Baranger (18) prepared several arylated esters from ethyl undecylenate and ethyl hydnocarpate and aromatic compounds in the presence of aluminum chloride. The purpose of this study was to make these compounds available for tests as therapeutic agents in the treatment of leprosy.

The olefinic compounds used were ω-undecylenic acid and the ethyl ester, ω-undecenyl acetate, ethyl hydnocarpate and ethyl allylmalonate. The aromatic compounds were benzene, anisole, phenylacetic acid, phenylpropionic acid, and benzyl cyanide. A mixture of isomers was obtained, and the product was generally an oil which could not be made to crystallize and

whose derivatives were likewise frequently oils. The authors noted that the double bond might migrate, to increase the number of isomers.

From the ethyl ω-undecylenate and benzene, two ethyl phenylundecylates were obtained by fractionation under reduced pressure, evidently the esters of ω-phenylundecylic and ω-1-phenylundecylic acids. Ethyl ω-bromoundecylate likewise produced a mixture of at least two isomers in the Friedel and Crafts reaction.

The following observations were made: (1) The yield increased the further the double bond was removed from the carboxyl group.

(2) For the same acid the yield increased if the acid was esterified.

(3) The yield of the monosubstituted derivative was greater if the para position was occupied (85% yield with anisole, 50% yield with benzene, in the case of undecylenic acid).

Phenylstearyl acetate and phenylstearyl alcohol have recently been made by the Friedel and Crafts reaction using oleyl acetate, benzene and aluminum chloride (51). This work was stimulated by the increasing economic importance of high molecular weight alcohols.

Both the phenylstearyl acetate (49% yield) and the alcohol obtained by hydrolysis were oils, apparently mixtures of the 9- and 10- isomers. The author noted his intention to continue his research and attempt to separate the isomers

as well as to apply the reaction to other aromatic hydrocarbons and study the products to be obtained on sulfonation.

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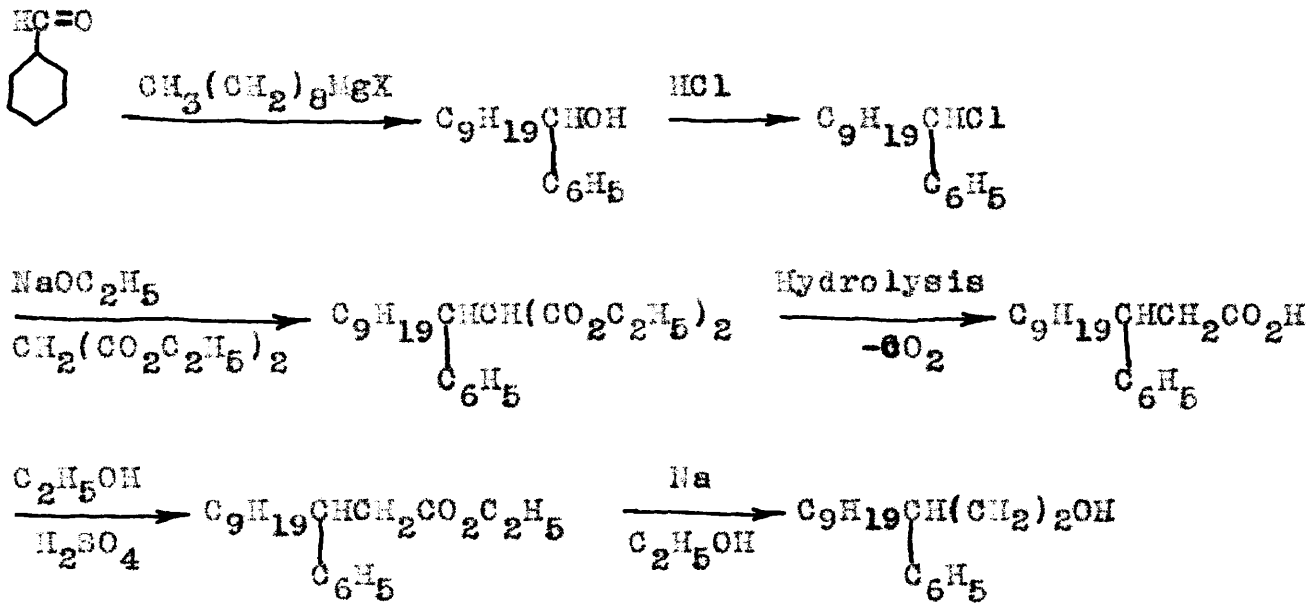
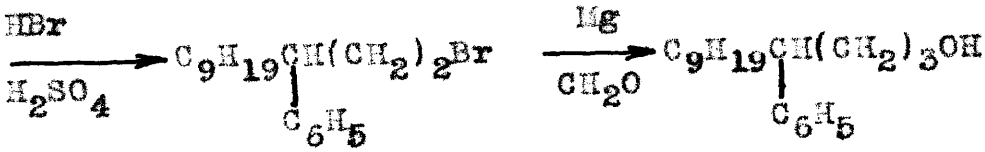
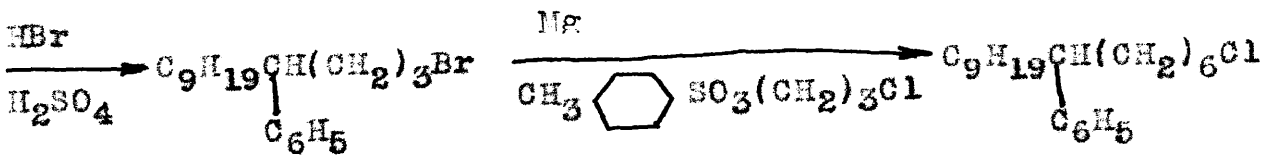
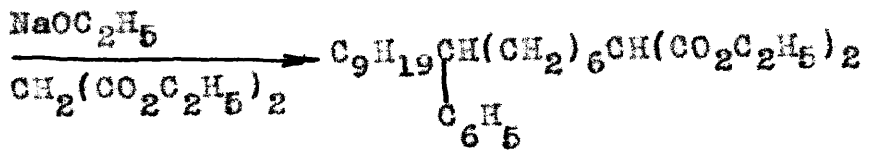
The above resumé completes the account of past contributions germane to the subject of this thesis. It should be noted, however, that arylstearic acids have been made by syntheses other than the Friedel and Crafts. The methods employed by Harmon and Marvel (24), although involving a long series of steps before the final product was obtained, led to the preparation of chemical individuals and not a mixture of isomers. The reactions leading to 9- and to 10-phenyloctadecanoic acids are illustrated:

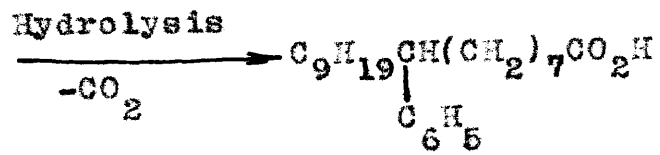
9-Phenyloctadecanoic Acid





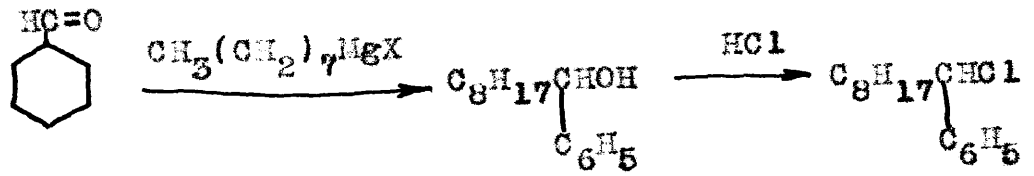


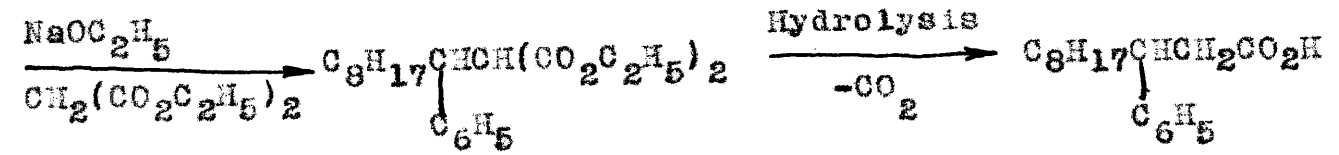


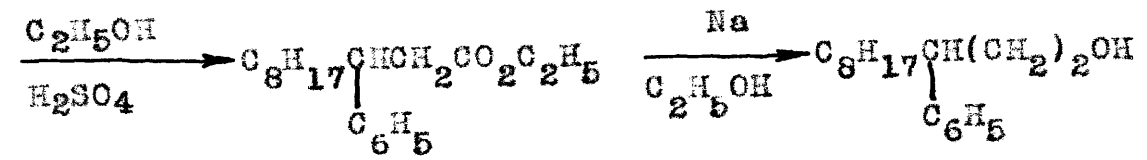


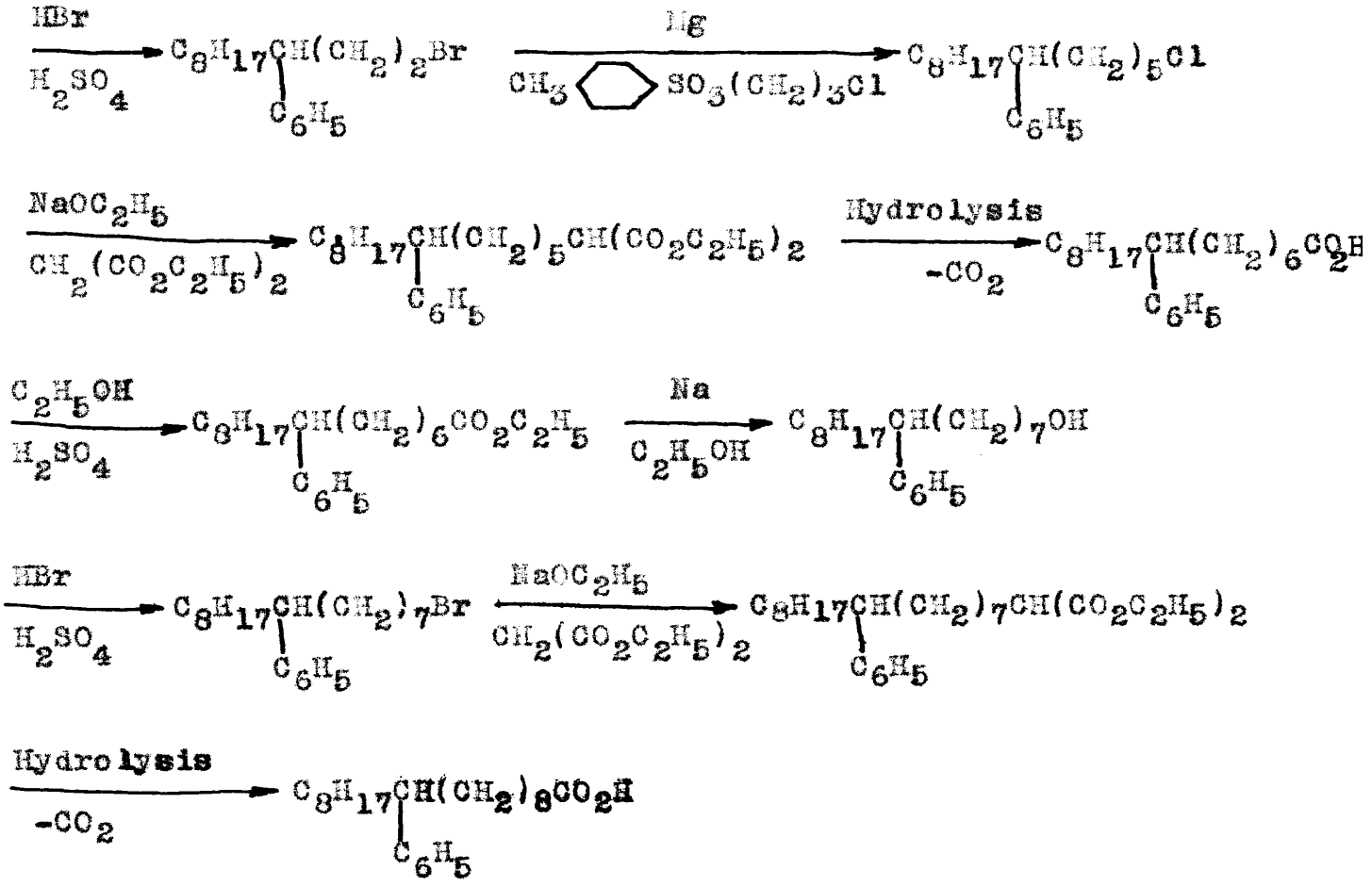
9-phenyloctadecanoic acid

10-Phenyloctadecanoic Acid









10-phenyloctadecanoic acid

Phenolic long chain fatty acids and alcohols have been prepared by Niederl and co-workers, from the phenol, the unsaturated acid or alcohol, and a cationoid condensing agent (sulfuric and glacial acetic acid mixtures). (38,39,40).

III. THEORETICAL

Mechanism

The alkylation of benzene by means of ethylene in the presence of aluminum chloride has been assumed to involve the intermediate formation of ethyl chloride (3). Such an interpretation has been reasonably satisfactory for reactions between an olefinic and an aromatic hydrocarbon. The reaction between ethylene and benzene slows down when too rapid a stream of ethylene carries away hydrogen chloride. The initial speed may be restored by passing in dry hydrogen chloride (5).

The extension of this mechanism to the reaction between an olefinic carboxylic acid and an aromatic hydrocarbon has not been as satisfactory. Eykman discarded this interpretation when he found that a number of α- and β-halogenofatty acids would not react in the Friedel and Crafts reaction. de Milt (8) found that the deliberate introduction of hydrogen chloride did not improve the yield of phenylstearic acid.

Marcusson (30) suggested a mechanism for the reaction between oleic acid and benzene as follows:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + AlCl_3 \longrightarrow CH_3(CH_2)_7\underset{Cl}{CH}\text{-}\underset{AlCl_2}{CH}(CH_2)_7COOH$$

The chlorine atom is then replaced by the phenyl radical with the evolution of HCl.

$$CH_3(CH_2)_7\underset{C_6H_5}{CH}\text{-}\underset{AlCl_2}{CH}(CH_2)_7COOH + HCl$$

The evolution of HCl is very marked during the reaction. On final hydrolysis the $-AlCl_2$ is displaced by hydrogen.

$$CH_3(CH_2)_7\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-(CH_2)_8COOH + Al\begin{matrix}OH\\Cl\\Cl\end{matrix}$$

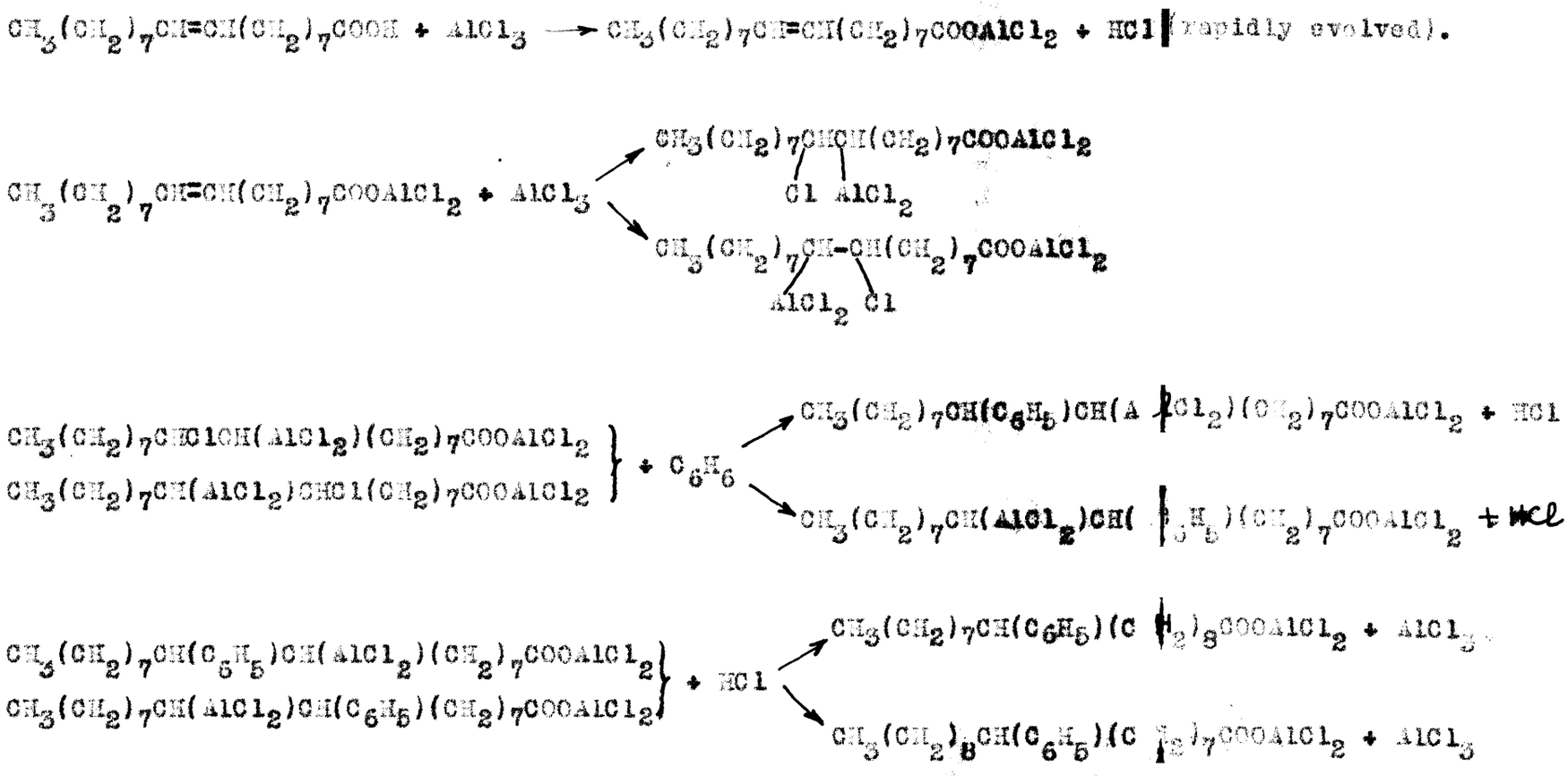
A very similar mechanism was proposed by de Milt (8). "The addition of HCl at the double bond of oleic acid takes place with very considerable difficulty; and it is, moreover not easy to see how important amounts of free hydrogen chloride could be present until after the reaction is under way. Perhaps the simplest assumption as to the mechanism would be that outlined in the following scheme:"

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow{AlCl_3} CH_3(CH_2)_7\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle AlCl_2}{\underset{|}{CH}}(CH_2)_7COOH$$

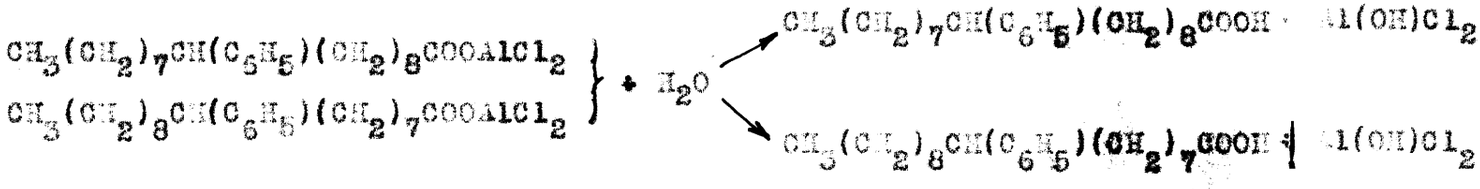
$$\xrightarrow{C_6H_6} CH_3(CH_2)_7\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-\underset{\displaystyle AlCl_2}{\underset{|}{CH}}(CH_2)_7COOH + HCl$$

$$CH_3(CH_2)_7\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-\underset{\displaystyle AlCl_2}{\underset{|}{CH}}(CH_2)_7COOH + HCl \rightarrow CH_3(CH_2)_7\underset{\displaystyle C_6H_5}{\underset{|}{CH}}(CH_2)_8COOH + AlCl_3$$

It is believed that a modification in the de Milt mechanism would account for the rapid evolution of HCl observed when olefinic acids are condensed, and, on the other hand, the hardly perceptible production of hydrogen chloride, when, instead, an olefinic ester is used:

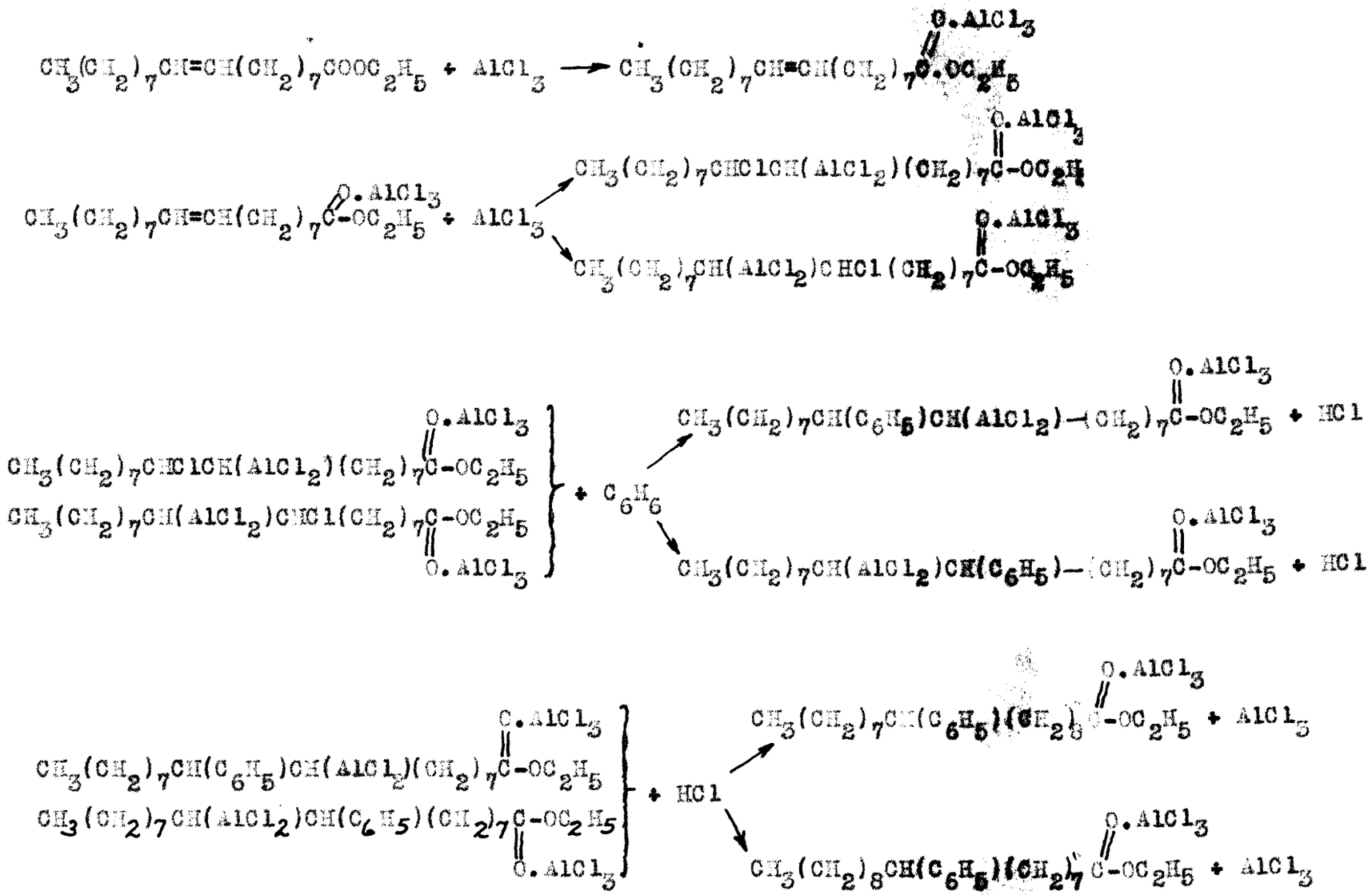


According to this scheme part of the $AlCl_3$ goes to form a mixed salt of aluminum with the almost immediate evolution of HCl, while a part becomes engaged in a catalytic reaction by means of which an arylstearic acid is prepared and $AlCl_3$ re-generated. On final hydrolysis the mixed salt is decomposed:



The application of this scheme to a reaction such as that of ethyl undecylenate, ethyl oleate, or oleyl acetate with benzene

differs from the case of an olefinic acid in that no significant evolution of HCl takes place:



On final hydrolysis the complex of the $AlCl_3$ with ethyl aryl-stearate is decomposed.

The need for an approximately stoichiometrical amount of $AlCl_3$ is explained in the case of carboxylic acids by the formation, perhaps only partially complete, of a mixed salt

and the rapid evolution of HCl. The evolution of HCl can be observed for instance if $AlCl_3$ be added to a solution of acetic or stearic acid in benzene, or to oleic acid in an inert solvent.

The reaction in the case of an ester is presumed to parallel that in which a ketone is formed in the Friedel and Crafts reaction. Complexes such as $CH_3COCl \cdot AlCl_3$, $CH_3COC_6H_5 \cdot AlCl_3$ and $C_6H_5COOC_2H_5 \cdot AlCl_3$ have been isolated (23,27,28,43,44,45).

Structure of the Arylstearic Acids

Oxidation. By oxidative degradation and from values of the molecular refractivity the structure of the arylstearic acids was partially established. No proof of the position of the aryl group in the chain can be offered. In each of the oxidation experiments the only product which could be isolated was the simple substituted aromatic acid. The identification of p-chlorobenzoic, p-bromobenzoic, p-anisic, terephthalic and p-phenylbenzoic acid from the oxidation of chlorophenylstearic, bromophenylstearic, methoxyphenylstearic, tolylstearic and xenylstearic acids respectively demonstrated the expected para orientation. It is possible the ortho derivative is also present, in amounts too small to be recognized by this method.

Molecular refractivity. The molecular refractivity of the oily arylstearic acids prepared was calculated from index of refraction and density measurements and the result compared with the sum of appropriate atomic refractivities. The agreement

was sufficiently close to confirm the structure assumed.

Migration of the double bond. If during the Friedel and Crafts reaction a migration of the double bond in oleic acid takes place, the number of possible arylstearic acids will increase. The final product would then be a more complex mixture of isomers and would be even more difficult to crystallize.

The migration of the double bond under the conditions used in carrying out the Friedel and Crafts reaction has not been demonstrated, but it is not impossible. Bauer and Panagoulias (4) established a shift of the double bond in oleic acid under the influence of zinc chloride, a catalyst having properties similar to aluminum chloride. Fifty grams of oleic acid, ten grams of zinc chloride, and one hundred grams of glacial acetic acid were refluxed sixteen hours. The isomer obtained was 10,11-octadecenoic acid.

Harmon and Marvel (24) concluded on comparing the p-bromophenacyl esters of 9- and of 10-phenyloctadecanoic acids with the ester of Nicolet and de Milt's acid that the phenylstearic acid prepared by the Friedel and Crafts reaction was roughly a mixture of equal parts of the two isomers. It can therefore be assumed that there is little or no migration of the double bond and the arylstearic acids here prepared are probably likewise mixtures of about equal amounts of the 9- and 10-isomers.

IV. EXPERIMENTAL

Materials

The oleic acid used was U. S. P. grade except in one experiment when C. P. oleic acid, free from linolic acid, was used. The ethyl oleate used in experiments designed to prepare ethyl arylstearates by the Friedel and Crafts reaction was (1) purchased from the Eastman Kodak Company, or (2) prepared from U. S. P. oleic acid and 95% ethyl alcohol by a modification of the method of Ellis (12). The data of Table I describes the ester.

TABLE I. ETHYL OLEATE

Source of the Ethyl Oleate	Sapon. Equiv.	Acidity, calc'd. as % oleic acid	Corr. Sapon. Equiv.	Iodine number	Distillation Range, °C.
Eastman Kodak (Technical)	304.8	3.62	317.0	79.0	- - -
Esterification of U.S.P. oleic acid. Ester fractionated under reduced pressure	308.3	.13	312.5	83.5	177-82/2 mm.

Theoretical saponification equivalent = 310.3
Theoretical Iodine number = 81.8
Corrected saponification equivalent calculated from the saponification equivalent and the free acid present.

The aluminum chloride used was a good commercial grade, yellow in color, and consisted of particles the size of a pea

(except in one experiment when C.P. aluminum chloride powder from the Eastman Kodak Company was used).

The aromatic compounds and solvents used were of good commercial grade and were purified by fractionation or by recrystallizing. Benzene was dried over sodium. Petroleum ether and petroleum naphtha were purified as follows: (1) agitation with portions of concentrated sulfuric acid until the sulfuric acid was no longer colored; (2) removal of acid by washing with water; (3) drying over calcium chloride; (4) agitation with powdered potassium permanganate; (5) filtration and distillation.

The Friedel and Crafts Reaction With Oleic Acid

1. Reactions using an excess of the aromatic reactant

The experiments are conveniently classified into three types: (1) those in which an excess of the aromatic compound being condensed constituted the solvent; (2) those in which an inert solvent was used; and (3) reactions without a solvent using the ball-mill reactor. Those of the first type were the most successful and are first reported.

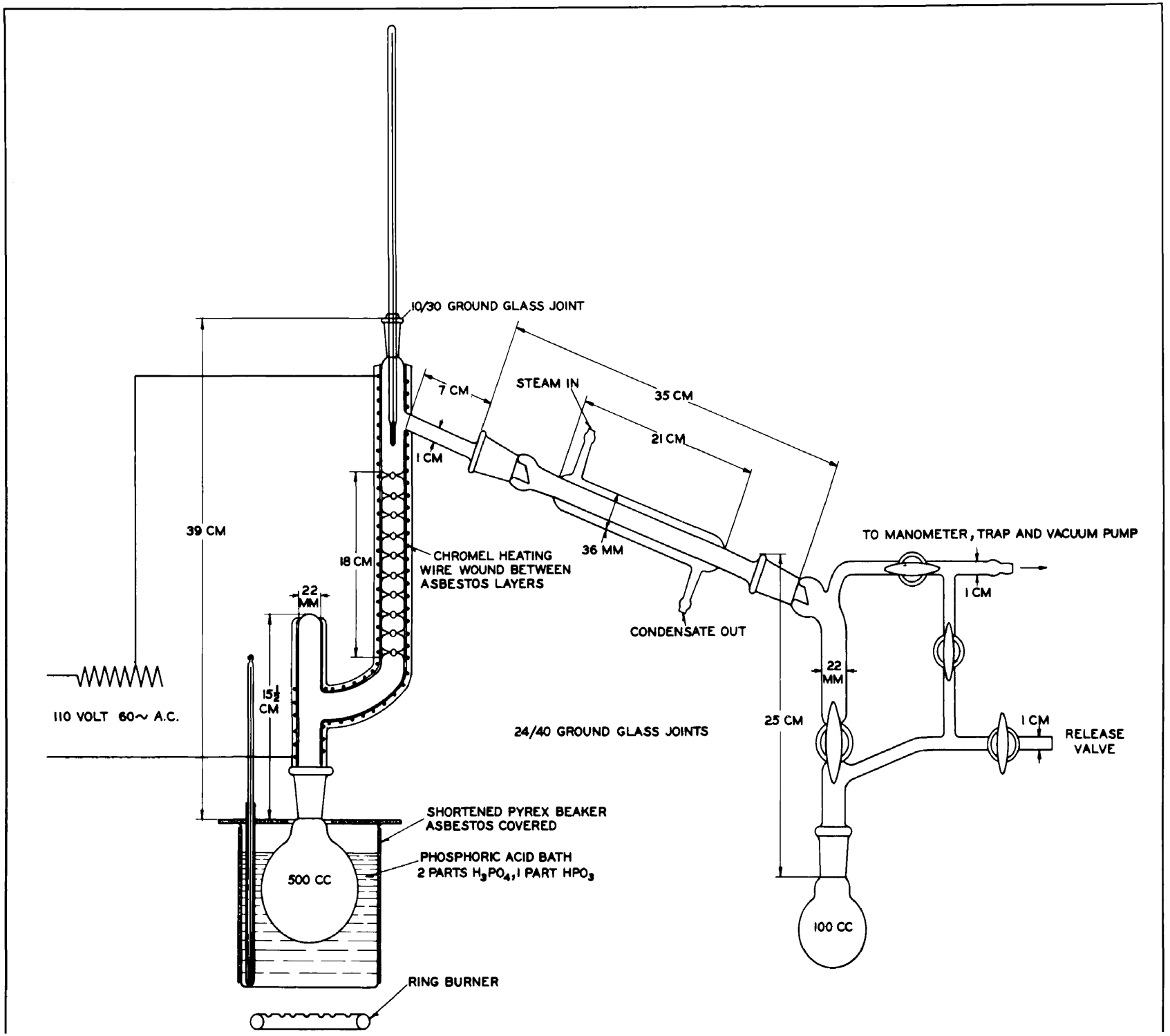
The reactions were carried out in 2-liter 3-neck flasks equipped with agitation and carrying a reflux condenser. It was convenient to use oleic acid in place of mercury in the

seal. The oil-bath equipped with thermostat control and designed to accommodate four experiments at one time has been described (21).

After the reaction was completed the cooled contents of the reaction flask were hydrolyzed in iced hydrochloric acid, the solvent layer separated and washed until free of hydrochloric acid, and then distilled with steam. The non-volatile oily residue was recovered with ether, the ether solution dried over anhydrous sodium sulfate, the solution filtered, the ether removed at reduced pressure on the water-bath, and the residual oil subjected to fractional distillation under about 1-2 mm. of mercury pressure (Figure 1). A phosphoric acid bath was used as the heating medium (7).

The lower fractions consisted largely of solid saturated fatty acids and had a neutralization equivalent of about 300. The next higher fractions contained the crude arylstearic acid, and the residue in the flask was apparently a polymerization product. (30, 31, 55) The crude arylstearic acid was further fractionated by one or more re-distillations. The final product was in each case a clear viscous oil, slightly yellow in color, which it has not been possible to obtain in crystalline form.

The method employed by Nicolet and de Milt was compared with that used by Schmidt and it was found the former was more satisfactory when it was the purpose to use an oleic acid of commerce (U.S.P. grade) and to isolate the product by distillation.


10/30 GROUND GLASS JOINT
7 CM
STEAM IN
35 CM
21 CM
1 CM
39 CM
18 CM
CHROMEL HEATING WIRE WOUND BETWEEN ASBESTOS LAYERS
36 MM
TO MANOMETER, TRAP AND VACUUM PUMP
1 CM
CONDENSATE OUT
22 MM
15½ CM
110 VOLT 60~ A.C.
24/40 GROUND GLASS JOINTS
25 CM
1 CM
RELEASE VALVE
SHORTENED PYREX BEAKER ASBESTOS COVERED
PHOSPHORIC ACID BATH
2 PARTS H_3PO_4, 1 PART HPO_3
500 CC
100 CC
RING BURNER

The manner of bringing the reactants together, the reaction temperature, and the solvent ratio were studied. The best results were obtained by adding aluminum chloride in portions at room temperature to a solution of oleic acid in the aromatic compound, the latter being present in large excess. The temperature was then raised to 80° and held there six hours. Mechanical agitation was continuous. These are the conditions used by Nicolet and de Milt in making phenylstearic acid and they were found to be the most suitable for making tolylstearic, xylylstearic, chlorophenylstearic and bromophenylstearic acids. Some experiments under different reaction conditions are summarized in Table II. Table III summarizes the optimum conditions for five arylstearic acids.

Attempts were made to condense o-dichlorobenzene and 1,2,4-trichlorobenzene with oleic acid but these were unsuccessful. The reactants were brought together in the usual manner, using excess of the aromatic compound as the solvent, and the reaction was carried out for six hours at 80°. A crude yield considerably lower than the usual was obtained. On vacuum distillation fractions of low neutralization equivalent were obtained (284.5 to 344.2) and the bulk of the material could not be distilled even at 300°. This suggested that the only reaction was one between oleic acid and aluminum chloride. Since o-dichlorobenzene and 1,2,4-trichlorobenzene are known to be less reactive than the aromatic compounds usually employed in the Friedel and Crafts reaction, these condensations were not further studied.

TABLE II. Comparison of Reaction Conditions

Expt	Aromatic Compound	Reaction Conditions	Grams Crude before dist'n	Yield on 2nd Distillation: b.p. °C./mm.	grams	%	Neut. Equiv. found	Neut. Equiv. theory
1[a]	Benzene	Oleic acid dissolved in benzene added to mixture of benzene and $AlCl_3$ slowly during 1 hr. at 80°; then 6 hrs. at 80°.	227	220-30/1	86	34	364.3	360.3
2	Benzene	$AlCl_3$ added to other reactants during 15 minutes at room temp. Then 6 hrs @ 80°	231	220-30/1	97	38	364.7	360.3
3	Toluene	ditto	240	232-8/1	101	38	380.8	374.3
4	Toluene	Toluene solution of oleic acid added during 40 min @ 73° to toluene suspension of $AlCl_3$; then 6 hrs. @ 80°	231	243-55/2	71	27	381.8	374.3
5	Toluene	$AlCl_3$ added during 15 minutes at room temperature; then 1½ hrs. @ 105°	217	222-40/1	90	34	386.7	374.3
6	Chloro-benzene	$AlCl_3$ added during 15 minutes at room temp; then 6 hrs. @ 80°	225	240-5/.5	71	25	399.1	394.8
7[b]	Chloro-benzene	ditto	180	231-8/.5	62	22	395.9	394.8
8[c]	Bromo-benzene	ditto	216	230-40/.2	39	13	434.5	439.2
9[d]	Bromo-benzene	ditto	218	241-50/2	68	22	439.3	439.2

[a] Represents the average of three experiments
[b] C. P. oleic acid used instead of U.S.P.
[c] Ratio mols Bromobenzene /Oleic acid = 4.496
[d] Ratio mols Bromobenzene /Oleic acid = 6.500
Ratio mols Benzene/Oleic acid=7.233; mols Toluene/Oleic acid=6.899; mols Chlorobenzene/Oleic acid=6.273.
200 grams Oleic acid (.7085 mols) and 100 grams $AlCl_3$(.75 mols) in each case.

TABLE III. Optimum Conditions for Five Arylstearic Acids

Acid	Mols Aromatic / Oleic acid	Grams crude before distillation	Yield on 2nd Distillation: b.p. °C.	grams	% theory	Neut. Equiv. found	Neut. Equiv. theory
Phenylstearic	7.233	231	220-30/1 mm.	97	38	364.7	360.3
Tolylstearic	6.899	240	232-38/1 mm.	101	38	380.8	374.3
Xylylstearic	6.653	233	235-36/.4 mm.	128	47	392.9	388.4
Chlorophenylstearic	6.275	225	240-45/.5 mm.	71	25	399.1	394.8
Bromophenylstearic	6.500	218	241-50/.2 mm.	68	22	439.3	439.2

Conditions: 100 grams $AlCl_3$ added in portions at room temperature during 15 minutes to solution of 200 grams oleic acid in excess of the aromatic compound. Temperature slowly raised to 80° and held there 6 hrs. Mechanical agitation continuous.

2. Use of an inert solvent

Anisole, xenene (diphenyl) and diphenyl ether were the compounds experimented with using an additional and inert material for the solvent.

Experiments with anisole. Three experiments, only one of which was successful (#3) may be described.

Experiment 1. To a solution containing 81 grams (.75 mol) of anisole and 200 grams of oleic acid dissolved in 400 cc. of carbon disulfide there was added 100 grams of aluminum

chloride during 45 minutes at 10-15°. The temperature was then kept at 25° for one hour, then 30-35° for two hours, and finally at 35-40° for one hour. The contents were hydrolyzed and treated as usual. Two hundred and eight grams of product were fractionally distilled at .5-1.5 mm. Decomposition was evident throughout the distillation. The oil previous to distillation was dark red and the distillate was red to violet and rapidly solidified. Acid vapors came through the pump and distillation was discontinued at 220°. The distillate had a neutralization equivalent of 313.0 (theoretical =390.3) and the residue gave positive tests for aluminum and chlorine and evolved hydrogen sulfide. These conditions were evidently ill-adapted to produce the desired arylstearic acid.

Experiment 2. To a solution containing 200 grams of anisole (1.851 mols) and 141 grams of oleic acid (.5 mol) dissolved in 300 grams of petroleum ether there was added 71 grams of aluminum chloride (.535 mol) during half an hour at 10°. The temperature was then kept at 15-20° for three and a half hours. Complete removal of mineral acid and inorganic material by hydrolysis, washing, introduction of steam and solution in alkali followed by reprecipitation with acid was practically impossible. The final product was a very sticky orange-yellow material, difficult to pour even when hot. It had a neutralization equivalent of 485.0. The presence of aluminum was shown by ignition. This material was not distilled since it could not be expected to yield the desired arylstearic acid.

Experiment 3. To 81 grams of anisole and 200 grams of oleic acid dissolved in 300 grams of petroleum ether there was added 100 grams of aluminum chloride during one hour at 10°. The temperature was raised and held at 10-20° for an hour and a half, then at 25° for three hours. The contents were hydrolyzed to yield 195 grams of oil. A fraction distilling at 240-280°/3 mm. was redistilled to give 40 grams b.p. 240-246°/2 mm. of neutralization equivalent 395.0 (theoretical = 390.3). Other evidence confirms this product as p-methoxyphenylstearic acid. Yield 14%.

Experiments with xenene. Experiment 1. To 109 grams of xenene and 200 grams of oleic acid dissolved in 400 cc. of carbon disulfide there was added 100 grams of aluminum chloride during an hour and a half at 15-30°. The temperature was then raised to 60° and held there one hour. The black reaction mass solidified during heating at 60° and agitation was ineffective. Most of the carbon disulfide was removed on the steam-bath, and steam introduced directly. The plastic yellow mass was washed, extracted with alcohol to remove xenene, boiled and macerated with concentrated hydrochloric acid to complete hydrolysis. The black oil was washed acid free and dried as usual. From 183 grams of product 40 grams b.p. 250-300°/2 mm. were obtained on fractional vacuum distillation. This fraction was orange with slight fluorescence and had a neutralization equivalent of 420.2 (theoretical = 436.4). It may have contained the desired xenylstearic acid but was

obviously quite impure. It became much darker in color on standing.

Experiment 2. To 218 grams of xenene and 200 grams of oleic acid dissolved in 600 grams of o-dichlorobenzene there was added 100 grams of aluminum chloride (Eastman, resublimed) during one half hour at 35-60°. Reaction was strongly exothermic. The temperature was raised to 80° and held there three hours. The contents were hydrolyzed and treated as usual. The crude product (204 grams) was fractionated under reduced pressure. After two re-distillations 36 grams b.p. 277-290°/1.5 mm., neutralization equivalent 441.4 (theoretical = 436.4) were obtained. Other evidence confirmed this product as -xenylstearic acid. Yield 12%.

3. Reactions without a solvent.

The Friedel and Crafts reaction can sometimes be effected without use of a solvent, by means of a ball-mill reactor. This procedure is frequently successful when each of the three reactants are solids, or even when one is a liquid (22). Success of this method depends upon the eventual formation of the aluminum chloride complex of the reaction product as a homogeneous dry powder which can then be delivered from the mill (20).

An attempt to use this procedure in preparing xenylstearic acid was unsuccessful.

Two hundred and thirty-one grams of xenene (1.5 mols) and 147 grams of aluminum chloride (1.1 mols) were ground

together in the mill at 25° for one hour. Two hundred and eighty-two grams of oleic acid (1 mol) was then added. The grinding noise immediately diminished and there was copious evolution of hydrogen chloride. The temperature was gradually raised to 30-35° and the mill was run for 22 hours. The product was a gummy, red-brown mass which was hydrolyzed with some difficulty and then treated as usual. On vacuum distillation at 1.5 mm. the bulk remained in the retort flask at 300°. A small fraction distilling at 220-300°/1.5 mm. had a neutralization equivalent of 348.

Behaviour of the reaction product suggested the only reaction was a polymerization of oleic acid by the aluminum chloride. Evidently preparation of xenylstearic acid in the ball-mill reactor is not feasible.

Experiments with diphenyl ether. An attempt to prepare phenoxyphenylstearic acid was unsuccessful.

To 170 grams of $(C_6H_5)_2O$ (1 mol) and 200 grams of oleic acid dissolved in 300 grams of tetrachloroethane there was added 100 grams of aluminum chloride during 15 minutes at room temperature. The temperature was then raised and heating and agitation continued for six hours at 80°. The contents were hydrolyzed and treated in the usual fashion. Either very little or no phenoxyphenylstearic acid was formed or else it cannot be distilled at or below 300° under 1 mm. pressure. One hundred and ninety-eight grams were submitted to vacuum distillation. The fraction b.p. 210-300°/1 mm. had a neutralization equivalent

of 305.9. The black viscous residue had a neutralization equivalent of 618.5. Theoretical for phenoxyphenylstearic acid = 452.4

The successful preparations of methoxyphenylstearic acid and xenylstearic acid are summarized in Table IV.

TABLE IV. Use of an Inert Solvent

Acid	Mols Aromatic / Oleic acid	Solvent	Grams Crude before distillation	Yield on final fractionation: b.p. °C.	grams	% theory	Neut. Equiv. found	Neut. Equiv. theory
p-Methoxyphenylstearic[a]	1.059	300 gms. Petroleum ether	203	240-46/2 mm.	40	14	395.0	390.3
p-Xenylstearic[b]	2.000	600 gms. o-Dichlorobenzene	210	277-90/1.5mm	36	12	441.4	436.4

Reaction Conditions:

[a] $AlCl_3$ added during 1 hr. at 10°; then temperature at 10-20° for 1½ hrs., finally at 25° for 3 hrs.

[b] Eastman resublimed $AlCl_3$ (powder) added during ½ hr. at 55-60°. Temperature then kept at 80° for 3 hrs.

In each case 200 grams oleic acid (.7085 mol) and 100 grams of $AlCl_3$ /(.75 mol) were used. Mechanical agitation continuous.

The Friedel and Crafts Reaction

With Ethyl Oleate

A number of experiments were carried out in an attempt

to prepare the ethyl arylstearate from ethyl oleate, aluminum chloride, and the aromatic compound, under conditions similar to those chosen for preparing the corresponding arylstearic acids. Ethyl tolylstearate was prepared in this manner but the results were not promising or else clearly unsuccessful in the case of bromobenzene, naphthalene, xenene, anisole and diphenyl ether.

The condensation of ethyl oleate with anisole was tried at lower temperatures, with petroleum ether as the solvent, but the product was largely unconverted ethyl oleate.

The ethyl tolylstearate of Table V was fractionated as follows:

Fraction	Range, °C./1 mm.	grams	Saponification Equiv.
1	205-12	16	- - - -
2	212-20	37	398.6
3	220-22	20	403.0

Molecular refractivity and analyses for carbon and hydrogen on fraction 3 agreed with the theoretical values for ethyl tolylstearate.

Oxidation

1. Catalytic oxidation

The catalytic oxidation of an arylstearic acid for the purpose of establishing the position of the aryl group was considered. Experiments with the catalyst manganese dioxide suspended in the arylstearic acid and air or oxygen as the

Table V. The Friedel and Crafts Reaction With Ethyl Oleate

Aromatic Compound	Mol Ratio: Aromatic / Ethyl Oleate	Solvent	Yield on 1st Distillation: Gms.	Range, °C.	Sap'n Equiv	% Acidity [c]	Corr. Sap'n Equiv	Theo. Sap'n Equiv.
Toluene [a]	9.554	---	87	216-30/2 mm	394.9	.48	398.0	402.4
Bromobenzene [a]	10.000	---	40	215-63/.5mm	422.6	.45	425.5	467.3
Anisole [b]	1.500	441 gms. -dichloro-benzene	73	230-65/2 mm	366.2	3.40	392.5	418.4
Diphenyl Ether [b]	1.500	"	16	225-80/1 mm	426.5	4.54	457.0	480.4
Naphthalene [b]	1.500	"	36	230-85/1 mm	426.5	2.60	446.0	438.4
Xenene [b]	1.500	"	44	235-80/1 mm	439.0	2.63	457.5	464.4
Xenene [a]	1.500	369 gms. nitro-benzene	18	213-300/1 mm	402.5	2.10	418.4	464.4
Xenene [a]	1.500	350 gms. Skelly-solve B	57	215-300/.5mm	423.2	.97	429.4	464.4

Conditions: $AlCl_3$ (.535 mol) added in portions during 15 minutes to the solution containing ethyl oleate (.500 mol). Temperature then raised to 80° and held there 6 hours. Mechanical agitation continuous. The reaction mass was hydrolyzed on ice and treated as in the arylstearic acid experiments.

[a] Ethyl oleate prepared by esterification of U. S. P. oleic acid.

[b] Eastman Kodak (Technical) Ethyl Oleate

[c] Acidity was calculated assuming the free acid was oleic acid. From this value the corrected saponification equivalent was obtained.

oxidizing agent, showed such a large and continuous evolution of carbon dioxide at various temperatures that the isolation of acids such as caprylic $CH_3(CH_2)_6COOH$, pelargonic $CH_3(CH_2)_7COOH$, suberic $(CH_2)_6(COOH)_2$, or azelaic $(CH_2)_7(COOH)_2$ was not feasible. Catalytic oxidation was used, however, to establish the orientation of a substituted arylstearic acid and was preferred to permanganate oxidation in the isolation of the p-anisic acid from methoxyphenylstearic acid. The manganese dioxide catalyst was kindly supplied by J. J. Stubbs and has been described (50). The oxidation was carried out by simply bubbling oxygen into a mixture of the catalyst and the arylstearic acid in a 500 CC. 3-neck flask equipped with a thermometer and carrying a lead-off tube for testing for carbon dioxide. The long tube with sintered glass disc for oxygen dispersion, described by Stubbs and Senseman (53) was tried but because of foaming the simpler apparatus was preferred.

At the end of the experiment a clear reddish oil was left (all of the catalyst had dissolved). The oil was subjected to repeated extraction with hot water, the aqueous extracts separated and extracted with ether, and the ether evaporated. Yellow crystals remaining, m.p. 178°, were redissolved in hot water and recrystallized on cooling. The product then had a melting point of 183°, and a mixed melting point with a known sample showed no depression. It was therefore p-anisic acid.

2. Oxidation with potassium permanganate.

Tolylstearic, chlorophenylstearic, bromophenylstearic,

and xenylstearic acids were oxidized by potassium permanganate to terephthalic, p-chlorobenzoic, p-bromobenzoic, and p-phenylbenzoic acids, respectively. These experiments are summarized in Table VI.

The arylstearic acid was converted to the potassium soap (in experiments 3 and 4) by neutralizing the alcoholic solution with alcoholic potassium hydroxide and evaporating the alcohol. The soap was then re-dissolved in hot water. All of the oxidations were carried out in a 1-liter 3-neck flask equipped with mechanical agitation and carrying a reflux condenser. Aqueous potassium permanganate could be added gradually through a dropping funnel. On completion of the run the excess of permanganate was destroyed with sulfur dioxide and the contents of the flask were filtered. The clear filtrate eventually obtained was acidified with sulfuric acid. From this point on the procedure was slightly different in each case.

Terephthalic acid. The white precipitate obtained on acidification was redissolved in hot sodium hydroxide. An oil appeared which was removed by adding ether and separating the aqueous alkaline solution, which was then again acidified, yielding a white precipitate which melted near 300°. The dried solid was esterified by the method of Nisson (41) a procedure giving better results than the use of phosphorus pentachloride. The white crystals obtained had the m.p. of dimethyl terephthalate, 140°, and the oxidation product was therefore terephthalic

Index of refraction was measured in an Abbe refractometer in a constant temperature room (20°C.). Density was likewise determined at 20°, from the expression

$$d_{4^\circ}^{20^\circ} = D_w \left(\frac{W_L - W}{W_w - W}\right) + .0012 \left(1 - \frac{W_L - W}{W_w - W}\right)$$

where D_w = density of water at 20° = .998255

W_L = observed weight of liquid + density bottle

W_w = " " " water + " "

W = " " " density bottle

and .0012 is the mean density of air.

The results are set forth in Table VII. The error is less than 1% in most cases. "In calculating the molecular refractive power of a substance of high molecular weight, the error involved in each atomic value is multiplied many times, so that the final result may differ by as much as two units from the observed value." (52).

Derivatives

Nicolet and de Milt noted a failure to obtain crystalline derivatives from phenylstearic acid (37). Numerous preparations were studied but in each case the products, as listed below, were viscous oils.

p-nitrobenzyl phenylstearate

phenylstearylamide

phenylstearylanilide

phenylstearyl- p -tolylanilide

TABLE VII. Molecular Refractivity

Compound	B.p. °C.	Neut. or Sap'n. Equiv.	Formula	$d_{4^o}^{20^o}$	$n_D^{20^o}$	Molecular Refractivity: found[a] R_f	Molecular Refractivity: calc'd. R_c	% error[b]
p-Tolyl-stearic acid	232-38/1 mm.	380.8	$C_{25}H_{42}O'O''(=)_3$	.9342	1.4921	116.28	115.59	.60
Ethyl Tolyl-stearate	220-22/1 mm.	408.0	$C_{27}H_{46}O\ O''(=)_3$	.9164	1.4828	125.55	124.94	.33
p-Chlorophenyl-stearic Acid	240-45/1 mm.	399.1	$C_{24}H_{39}O'O''Cl\ (=)_3$	.9964	1.4999	116.49	115.83	.57
p-Bromophenyl-stearic Acid	241-50/.2 mm.	439.3	$C_{24}H_{39}O'O''Br(=)_3$	1.0924	1.5067	119.60	118.73	.75
p-Methoxyphenyl-stearic Acid	240-46/2 mm.	395.0	$C_{25}H_{42}O'O''O(=)_3$	.9642	1.4942	117.90	117.23	.57
p-Xenyl-stearic Acid	277-90/1.5 mm	441.4	$C_{30}H_{44}O'O''(=)_6$	.9800	1.5297	137.37	135.07	1.63
Xylyl-stearic Acid	235-36/.4 mm	392.9	$C_{26}H_{44}O'O''(=)_3$	.9350	1.4943	120.98	120.20	.65

[a] From the Lorenz-Lorentz formula, $R_f = \frac{M(n^2 - 1)}{d(n^2 + 2)}$

[b] $\%\text{error} = \frac{(R_f - R_c)100}{R_c}$

phenylstearyl- a-naphthylamide

dinitrophenylstearic acid

diaminophenylstearic acid

diacetylaminophenylstearic acid

dibenzoylaminophenylstearic acid

tribromodiaminophenylstearic acid

Later, Harmon and Marvel prepared the ester of this acid, p-bromophenacyl phenylstearate, m.p. 79-82°, after fourteen recrystallizations (24). This had been the only successful preparation of a solid derivative (with the exclusion of metal salts) of arylstearic acids obtained from oleic acid by the Friedel and Crafts reaction.

Schlutius (48) was unsuccessful when he attempted to characterize naphthylstearic acid as the amide, and again when he tried to make naphthylstearyl aldehyde from the acid chloride, with the purpose of obtaining crystalline derivatives of the aldehyde.

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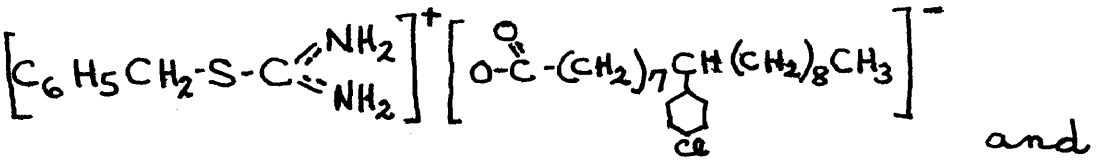
One of the arylstearic acids of this thesis was examined with the purpose of forming a solid derivative. The reagents p-bromophenacyl bromide (25) and p-phenylphenacyl bromide (10) were tried in an attempt to characterize p-chlorophenylstearic acid. The method of Kimura (26) was employed. The products, although precipitated as white semi-

crystalline solids on storing the alcoholic solution in the ice-box, were slowly converted to oils during the process of filtering at room temperature.

Another reagent, S-benzylthiuronium chloride (9) was selected and the salt S-benzylthiuronium p-chlorophenylstearate formed after the method of Anderson (1). The product is a white solid, shown to be crystalline when examined under the microscope. The melting point is 129°. It was analyzed as described under Analytical Methods. This salt is probably a mixture of the two isomers:



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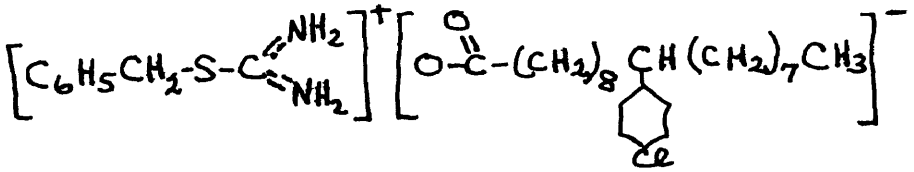

Analytical Methods

1. Neutralization Equivalent.

A one gram sample was dissolved in 75 cc. of neutralized alcohol, 2-4 drops of a 1% solution of neutralized phenolphthalein were added, and the alcoholic solution titrated with N/10 NaOH to a faint pink. The neutralization equivalents obtained have been tabulated. (Tables II, III, IV, VII).

2. Saponification Equivalent.

To a one gram sample 10 cc. of .6 N alcoholic KOH and 40 cc of alcohol were added. The flask was equipped with an air condenser and placed on the steam bath to boil

gently for half an hour. The excess of KOH was titrated with N/10 HCl to a phenolphthalein end-point. Blanks were run under parallel conditions. The saponification equivalents obtained have been compared with the theoretical in Tables I, V and VII.

3. Iodine number (Hanus method--Official). (2)

The Iodine numbers of the arylstearic acids and of ethyl tolylstearate were very low (about 1.0 or 2.0) and these have not been tabulated.

4. Halogen.

Halogen was determined gravimetrically on samples of chlorophenyl- and bromophenylstearic acids, using the Parr bomb and following the customary procedure (17).

5. Carbon and Hydrogen

The per cent of carbon and hydrogen in the arylstearic acids and in ethyl tolylstearate was determined by combustion, using the apparatus of Phillips and Hellbach (46). The results are set forth in Table IX.

6. Nitrogen.

Per cent nitrogen was determined on samples of S-benzylthiuronium p-chlorophenylstearate by a semi-micro modification of the Kjeldahl method. Apparatus similar to that of Parnas and Wagner (42) was employed. The indicator used was Benzoyl Auramine G (47). Blanks were run to correct for nitrogen in the reagents and the 1/3 cigarette paper used to weigh the sample.

Grams sample = .0368, .0305, .0303; cc. .03322 NNaOH used in back titration = 5.46, 6.12, 6.12; cc. 03322 NNaOH used in back titration of blank = 9.32; % N found = 4.88, 4.88, 4.92. Theoretical % N in $C_{32}H_{49}O_2N_2ClS$ = 5.00.

TABLE VIII. Halogen Determinations.

Acid	Neut. Equiv.	B.p. °C. at 2mm.	#	Grams Sample	Weight AgX^a	% Halogen found	% Halogen theo.
p-Chlorophenyl-stearic $C_{24}H_{39}O_2Cl$	394.2	217-23	(1)	.3046	.1096	8.90	8.98
			(2)	.3115	.1117	8.87	8.98
p-Bromophenyl-stearic $C_{24}H_{39}O_2Br$	439.3	241-50	(1)	.2870	.1204	17.65	18.20
			(2)	.3271	.1375	17.69	18.20
			(3)	.2886	.1218	17.96	18.20

[a] These are the weights of the precipitate after .0013 grams (precipitate found in blank) had been subtracted.

TABLE IX Combustions

Compound	#	Grams Sample	Grams H_2O	Grams CO_2	Found %H	Found %C	Theoretical %H	Theoretical %C
p-Tolylstearic Acid b.p. 232-8°/1; M.W.=380.8	1	.0645	.0658	.1892	11.42	80.00	11.31	80.14
"	2	.0863	.0882	.2533	11.44	80.05	11.31	80.14
Ethyl Tolylstearate b.p. 220-2°/1; M.W.=403.0	1	.0935	.0976	.2762	11.68	80.57	11.52	80.52
"	2	.0962	.1005	.2844	11.69	80.63	11.52	80.52
p-Chlorophenylstearic Acid b.p. 217-23°/.2; M.W.=394.2	1	.0866	.0768	.2312	9.92	72.81	9.96	72.95
"	2	.0815	.0732	.2176	10.05	72.82	9.96	72.95
p-Bromophenylstearic Acid b.p. 241-40°/.2; M.W.=439.3	1	.0746	.0605	.1798	9.08	65.73	8.95	65.57
"	2	.1103	.0901	.2661	9.14	65.80	8.95	65.57
"	3	.1093	.0888	.2656	9.09	65.78	8.95	65.57
p-Methoxyphenylstearic Acid b.p. 240-5°/2; M.W.= 395.0	1	.0712	.0694	.2004	10.91	76.77	10.85	76.86
"	2	.0711	.0693	.1997	10.91	76.60	10.85	76.86
p-Xenylstearic Acid b.p.277/1.0--290/1.5; M.W. = 441.4	1	.0938	.0861	.2824	10.27	82.11	10.16	82.50
"	2	.1054	.0966	.3173	10.26	82.11	10.16	82.50
"	3	.0875	.0799	.2640	10.22	82.29	10.16	82.50
Xylylstearic Acid b.p. 214-6°/.2; M.W.= 390.2	1	.1051	.1086	.3090	11.56	80.19	11.42	80.54
"	2	.1145	.1169	.3366	11.44	80.32	11.42	80.54

V. SUMMARY

Five new arylstearic acids, p-methoxyphenylstearic, p-tolylstearic, p-chlorophenylstearic, p-bromophenylstearic and p-xenylstearic have been prepared from oleic acid and the appropriate aromatic compound in the presence of aluminum chloride. Ethyl oleate behaves similarly in such a reaction. The acids in all cases are viscous oils after isolation under reduced pressure, probably because they represent a mixture of the 9- and 10-arylstearic acids. Partial proof of structure has been obtained by oxidation to the simple substituted aromatic acid and by values of molecular refractivities. The acids form solid derivatives with S-benzylthiuronium chloride. The arylstearic acids may find uses (1) as an addition agent to lubricants (2) as soaps by conversion to salts of triethanolamine or related bases (3) as wetting agents by conversion to a sulfonated derivative (4) as synthetic waxes by conversion to high molecular weight esters.

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