# KETONIZATION OF STEARIC ACID AND THE PREPARATION OF DI-18-PENTATRIACONTYL OXALATE

By

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# CONTENTS

# I

# INTRODUCTION

The object of this research was the preparation of di-18-pentatriacontyl oxalate by a series of reactions starting with stearic acid.

Stearic acid is one of the typical fatty acids occurring in natural fats. In recent years an abundance of these fatty acids have become available for use. The ease of conversion of these acids to ketones and other reactive compounds should make possible a number of new products. Although a large number of papers have been published on this subject many gaps exist in the literature. Should the same effort be given to the chemistry of fatty acids and related compounds that was given to coal tar products, it is safe to predict that many new uses will be found for these materials.

The major portion of this work is concerned with preparation of stearone from stearic acid by heating in the presence of iron or magnesium oxide catalysts. A trouble free process was worked out based on new knowledge concerning this reaction. This reduction of stearone to 18-pentatriacontanol is presented, as well as a procedure for the esterification of this alcohol with oxalic acid to prepare a new compound.

This work is a part of a more extensive program to prepare a series of esters of dibasic acids and alcohols derived from fatty acids, and the condensation of these esters to higher molecular compounds. It is hoped that this work will help to inspire others to carry on in this fascinating area of chemistry.

## II

## HISTORICAL AND THEORETICAL

### Preparation of Stearone

Stearic acid is obtained from natural fats. Chemists began experimenting with it and other fatty acids at a very early date. Jahresbericht für Chemie[1] states that J. Heintz used stearic acid to prepare stearone in 1855. Heintz's publication was not available for reference, but he is reported to have obtained stearone in poor yields by the distillation of stearic acid alone or with lime. By recrystallization from ether he got a compound which melted at 87.8°C.

Krafft,[2] in 1882, prepared stearone by distilling stearic acid and lime, obtaining the pure product (M.P. 88.4°C.) in less than half the theoretical yield. He found purification of the stearone to be very difficult.

Phosphoric anhydride was used by Kipping[3] as a catalyst in the conversion of stearic acid to stearone.

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[1] J. Heintz, Pogg. Ann., 96, 65. Ref. cit. Jahres. Chem., 516 (1855).

[2] F. Krafft, Ber., 15, 1715 (1882).

[3] F. S. Kipping, J. Chem. Soc., 57, 537 (1890).

He obtained 41 per cent yield of the crude ketone by heating pure stearic acid at 210°C. and adding phosphoric anhydride in small portions. The stearone was purified by recrystallization from ethyl alcohol. It melted at 88.0°C.

When commercial stearic acid was used, a ketone was obtained which melted 75° to 76°C. and could not be purified by repeated recrystallization.

Kipping prepared the oxime derivative of stearone, melting point 63°C.

Stearone was prepared and studied by Hansen[4] in 1909. He reported that the purified ketone melted at 88.4°C. and vaporized at 58°C. under the best vacuum obtainable.

Iron was used as a catalyst for the formation of stearone from stearic acid by Easterfield and Taylor.[5] Heating the acid with powdered cast-iron turnings to 360° to 370°C. for a period of three hours gave an 80 per cent yield of crude stearone melting at 85°C. The

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[4] C. J. Hansen, Ber. 42, 213 (1909).

[5] T. H. Easterfield and C. M. Taylor, J. Chem. Soc., 99, 2299 (1911).

impure ketone was recrystallized twice from light petroleum. It melted at 88°C.

These authors theorize that the ferrous salt of stearic acid is first formed and that this then undergoes decomposition forming stearone. To substantiate this theory, ketonization reactions were run using varying amounts of iron. With a decrease in the amount of iron, below the amount theoretically required for ferrous salt formation, there occurred a related decrease in yield of stearone. (Curtis et al.[6] reported that the amount of catalyst effects reaction time, but not yield.) The use of iron in excess of the theoretical quantity did not improve the yield of ketone. They found that when pure ferrous stearate is heated to 360°C. it slowly decomposes and yields 60 per cent stearone. When stearic acid was heated with 100 per cent of the theoretical quantity of iron at 360°C. a 60 per cent yield of stearone was also obtained. Aluminum and manganese gave approximately the same results.

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6. R. G. Curtis, A. G. Dobson, and H. H. Hatt, _J. Soc. Chem. Ind. (London)_, _66_, 402-7 (1947).

Grün and his co-workers[7] investigated numerous catalysts for the ketonization of stearic acid. Using silicates, aluminum, manganese, cadnium sulfide, and oxides of titanium, thorium, copper and iron, they never got over a 30 per cent yield by carrying the reaction at 360°C. for six hours. They then reported a 91 per cent yield of stearone by merely heating stearic acid in an iron pot for four hours. By heating further or adding small amounts of iron, quantative yields were obtained. Stearic acid, when reacted in small amounts was completely ketonized in 3 hours at 300°C. It appeared that the hot iron walls of the container was an excellent catalyst for ketonization.

The products of the ketonizations were recrystallized from ethyl alcohol. Stearone which melted at 88.5°C. was reported, along with the oxime derivative which melted at 66° to 67°C.

A phenomenon was observed by Grün, as well as by other investigators, that of vigorous frothing at some point in the ketonization reaction. (Vigorous frothing here means the rapid development of foam to such an

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[7] A. D. Grun, *et al.*, *Z angew. Chem.*, 39, 421-3 (1926).

extent that it overflows the raction vessel if the vessel is filled above one tenth its capacity.) These authors partially controlled frothing by using a large reaction container to allow for expansion of the material, by stirring, and by increasing the temperature slowly.

Kino[8] reported that only iron and magnesium compounds were catalysts for ketonization of fatty acids. This conclusion was based on observations of effects of a large variety of metals and their oxides on stearic acid when heated together for 1 to 6 hours. In a subsequent report Kino[9] reported that frothing during ketonization could be prevented by use of heavy metal soaps. Others working with this reaction were unable to verify this action of heavy metal soaps.

The use of $Al_2O_3$ or $Al(OH)_3$ as catalyst and a temperature of 330° to 360°C. was reported by Kino and Kato[10] to give a ketonization reaction in which no frothing appeared.

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[8] K. Kino, J. Soc. Chem. Ind. Japan, 40, Suppl. Binding, 194-5 (1937). Ref. cit. C. A., 31, 6614 (1937).

[9] Ibid., 32, 1961 (1938).

[10] K. Kino and S. Kato, Bull. Inst. Phy. Chem. Research (Tokyo), 19, 179-82 (1940). Ref. cit., C. A. 34, 6220 (1940).

Curtis and co-workers[11] repeated much work done previously on ketonization reactions. They reported that liquid phase ketonization gave better results than gas phase reactions. In the liquid phase there was much less decomposition and the reaction conditions were simpler. Using liquid phase reactions they carried out careful experiments to investigate the frothing phenomenon.

Two mechanisms were suggested by Curtis to account for various observations made during ketonization. First, the use of an excess of catalyst allows the reaction to proceed according to the equations (using MgO as catalyst)

(1) $2RCH_2COOH + MgO \longrightarrow (RCH_2COO)_2Mg + H_2O$

(2) $(RCH_2COO)_2Mg \longrightarrow (RCH_2)_2CO + MgO + CO_2$.

According to this reaction the liberation of carbon dioxide results from the decomposition of the magnesium soap (2), a typical autocatalytic reaction. The liberation of carbon dioxide has no sharp changes in rate. However, the use of the catalyst in amounts less than the equivalent for salt formation causes a slow liberation of carbon dioxide at first then a sudden increase in rate of this liberation after a period of heating. Curtis proposes

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[11] R. G. Curtis, *et al.*, *loc. cit.*

that in this case reaction (2) be replaced by reactions (3) to (6).

(3) $(RCH_2COO)_2Mg \longrightarrow RCH_2COCHRCOOMgOH$

(4a) $RCH_2COCHRCOOMgOH + RCH_2COOH \longrightarrow RCH_2COCHRCOOMgOCOCH_2R + H_2O$

(4b) $RCH_2COCHRCOOMgOCOCH_2R + RCH_2COOH \longrightarrow RCH_2COCHRCOOH + (RCH_2COO)_2Mg$

(5) $RCH_2COCHRCOOMgOH \longrightarrow (RCH_2)_2CO + MgO + CO_2$

(6) $RCH_2COCHRCOOH \longrightarrow (RCH_2)_2CO + CO_2$

Experimental evidence was given by Curtis to support this idea that keto-acid salts are formed when an excess of the acid is present and then as soon as this excess acid is used up the reaction proceeds according to (2). He concluded that the magnesium oxide catalyzes the formation of the keto-acid salt and that formation of this salt is the rate determining step. He regarded uncontrollable frothing as resulting from the sudden passage from a slow, steady rate of evolution of carbon dioxide (decomposition of keto-acid and kito-acid salt) to a more rapid rate (decomposition of metal soap) when the catalyst became in excess.

In his experiments, Curtis controlled frothing by heating the catalyst to the reaction temperature and adding the fatty acid in portions so that the catalyst was always present in excess. He reported that when the total amount of acid and catalyst were heated together he got frothing in all runs in which the temperature was maintained above 300°C. The use of iron as a catalyst led to frothing even when the iron was heated and the acid added in portions.

A number of other investigators have reported work on the preparation of stearone. McCorkle[12] prepared 2-hexadecyl- 3-oxoarachidamide by treating stearonitrile with sulfuric acid. Hydrolysis of this amide produced stearone. Hoffman and co-workers[13] prepared stearone by passing stearic acid over a manganese chromite catalyst at 410°C. Becker and Strating[14] prepared stearone melting 88.7° to 88.9°C. by heating stearic acid with iron

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[12] M. R. McCorkle, Iowa State Coll. J. Sci., 14, 64-6 (1939) Ref. cit., C. A., 34, 6220 (1940).

[13] E. J. Hoffman, A. W. Ralston, and G. E. Ziegler, J. Phys. Chem., 43, 301-7 (1939).

[14] H. J. Becker and J. Stating, Rec. trav. chim., 59, 933-46 (1940) Ref. cit., C. A. 35, 4727 (1941).

at 300°C. Franke and co-workers[15] obtained stearone as a by-product in working with methyl stearate. Toyoda[16] prepared pure stearone by the decarboxylation of sodium salts of stearic acid, and Clement[17] prepared stearone (M.P. 88° to 89°C.) by the decomposition of ethyl alpha-stearylstearate at 140°C.

## Reduction of Stearone to 18-Pentatriacontanol

Comparatively mild reduction conditions must be used with stearone to prepare the corresponding secondary alcohol, otherwise the reduction will proceed to the hydrocarbon.

Easterfield and Taylor[18] were first in reporting the preparation of 18-pentatriacontanol (diheptadecylcarbinol). They attempted the reduction of stearone with sodium and ethyl alcohol without success but obtained a

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[15] W. Franke, *et al.*, *Ann.*, *561*, 98-106 (1948), C. A., *43*, 2940 (1949).

[16] R. Toyoda, *Bull. Inst. Chem. Research, Kyota Univ.*, *21*, 32-40 (1950) Ref. cit., C. A., *48*, 4436 (1954).

[17] R. Clement, *Compt. rend.*, *236*, 718-720 (1953) Ref. cit. C. A., *48*, 119 (1954).

[18] Easterfield and Taylor, *loc. cit.*

compound melting at 89.5°C. by 8 hours refluxing with sodium and amyl alcohol. The acetate derivative of this compound melted at 54° to 61°C. (no sharp melting point).

Grün[19] reported an elegant method of reduction of ketones with a mixture of sodium hydroxide and a primary alcohol. The reaction is represented by the equation $2R_2CO + C_2H_5OH + NaOH \longrightarrow 2R_2CHOH + CH_3COONa$. It was carried out in a copper-lined autoclave at 10 atmospheres pressure and 300°C. The pressure was necessary to contain the ethyl alcohol. They reported that the use of ethyl alcohol gave a 90 per cent yield and n-amyl alcohol gave a 96 to 97 per cent yield after 6 to 8 hours treatment.

Butyl alcohol and sodium were utilized by Kino[20] in the reduction of stearone.

Dryden[21] reduced stearone with aluminum isopropoxide in isopropyl alcohol. He reported that the alcohol melted at 89.8° to 90.8°C.

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[19] A. D. Grun _et al._, _loc. cit._

[20] K. Kino, _J. Soc. Chem. Ind., Japan_, _42_, Suppl. Binding, 187 (1939).

[21] J. S. Dryden, _Australian J. Sci. Research A 5_, 661-70 (1952) C. A., _47_, 3060 (1953).

## Esterification of 18-Pentatriacontanol

An acetyl ester was prepared by Easterfield,[22] the person who first reported the preparation of 18-pentatriacontanol. He refluxed the alcohol with acetic anhydride for two hours and got a compound which melted at 54° to 61°C.

Grün[23] also used acetic anhydride to prepare the acetate ester of 18-pentatriacontanol. His product melted at 58° to 59°C. He also prepared a series of esters from lauric, myristic, palmitic, and stearic acids. Ordinary methods of esterification were found to be inadequate, so Grun used a method in which the alcohol was warmed on a water bath, carbon dioxide passed through, and an excess of the acid chloride added.

No work has been reported on esters of dibasic acids and 18-pentatriacontanol or closely related homologs.

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22. Easterfield and Taylor, loc. cit., p. 2300.

23. A. D. Grün et al., loc. cit., pp. 421-427.

# III

# EXPERIMENTAL

## Preparation of Stearone from Stearic Acid

Stearone was prepared by the general method of Grün[1] using iron as a catalyst. 46.8 g. (0.165 moles) of commercial stearic acid (Baker and Adamson, N. F.) and 4.7 g. (0.084 g. at) of powdered iron (Mallinckrodt, Analytical Reagent) were placed in a three-necked, 500-ml. flask equipped with a half-moon stirrer and an air condenser. The reaction flask was placed in a salt bath ($NaNO_3$) at 340°C., and the mixture stirred vigorously as the temperature rose. At a temperature of approximately 250°C., the mixture became very viscous, necessitating an increase in the speed of the stirrer to maintain the desired amount of mixing, and to permit carbon dioxide to escape more easily. The temperature of the reaction mixture increased rather rapidly to 320°C., some foam (but no excessive frothing) then appeared. The mixture became less viscous (requiring less stirring) and the

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[1] A. D. Grun, <u>et al</u>., <u>Z</u>. <u>angew</u>. <u>Chem</u>., <u>39</u>, 422 (1926).

temperature dropped to 310°C. By increasing the temperature of the salt bath to 355°C., the temperature of the reaction mixture was raised to 320°C. After heating for one hour under these conditions the acid number was reduced from 200 to 14.1. Heating the mixture for 1 hour more lowered the acid number to 2.1. The dark, greasy solid which formed upon cooling weighed 44.5 g. It was boiled with dilute hydrochloric acid to decompose any remaining metal salts, then with dilute sodium hydroxide to remove any unreacted stearic acid. The crude ketone then weighed 40.5 g. (0.082 mole- 98.3 per cent yield, including the substance used in running acid numbers). It was dissolved in ethyl alcohol and decolorized with animal charcoal. After three recrystallizations from ethyl alcohol the stearone melted at 80° to 81°C.

The above product was subjected to a number of purifications procedures including fractional crystallization, fractional freezing, and sublimation under reduced pressure using a cold finger condenser. The melting point remained constant, although much lower than the accepted value of 88° to 89°C. This indicated that the separation of a mixture of palmitone, stearone, and related unsymetrical ketones would be very difficult. It is supposed that an eutectic mixture is formed.

The ketonization of stearic acid was carried out varying the amounts of iron used for catalyst along with different reaction temperatures in order to determine the conditions which would give the best yields in the shortest time. The acid number was determined periodically during the course of the reaction. Typical runs are summarized in Table 1. In Figure 1, acid numbers from these runs are plotted against time. (The iron is used in proportional equivalents for the conversion of the acid to the ferrous salt.)

Figure 1 shows that the use of the equivalent amount of iron and a temperature of 320°C. gave the shortest reaction time of those runs illustrated.

Other runs indicated that iron in excess of the amount required for soap formation does not aid the reaction. A higher reaction temperature gave a much poorer product. Lower temperatures extended the reaction time considerably.

In all cases where vigorous stirring and rapid increase in temperature were not performed the reaction frothed excessively. The frothing usually occurred at a temperature of 300° to 320°C.

Magnesium oxide was used instead of iron for the catalyst in the preparation of stearone. In a number of

## Table 1

## KETONIZATION REACTIONS USING IRON

| Run Number | Reaction Temperature | Amount of Catalyst (Equiv.) | Reaction Time (Hrs.) | Acid Number |
|---|---|---|---|---|
| 4 | 300°C. | 0.2 | 1 | 187 |
| | | | 2 | 171 |
| | | | 4 | 128 |
| | | | 6 | 4.4 |
| | | | 7½ | 1.2 |
| 5 | 330°C. | 0.2 | ½ | 191 |
| | | | 2½ | 139 |
| | | | 4½ | 3.4 |
| 6 | 240°C. | None* | 1 | 196 |
| | | | 2 | 170 |
| | | | 5 | 123 |
| | | | 9 | 7.2 |
| 10 | 320°C. | 1.0 | 1 | 14.1 |
| | | | | .45 |

*This reaction was run in an iron vessel, the walls of the container serving as the only catalyst.

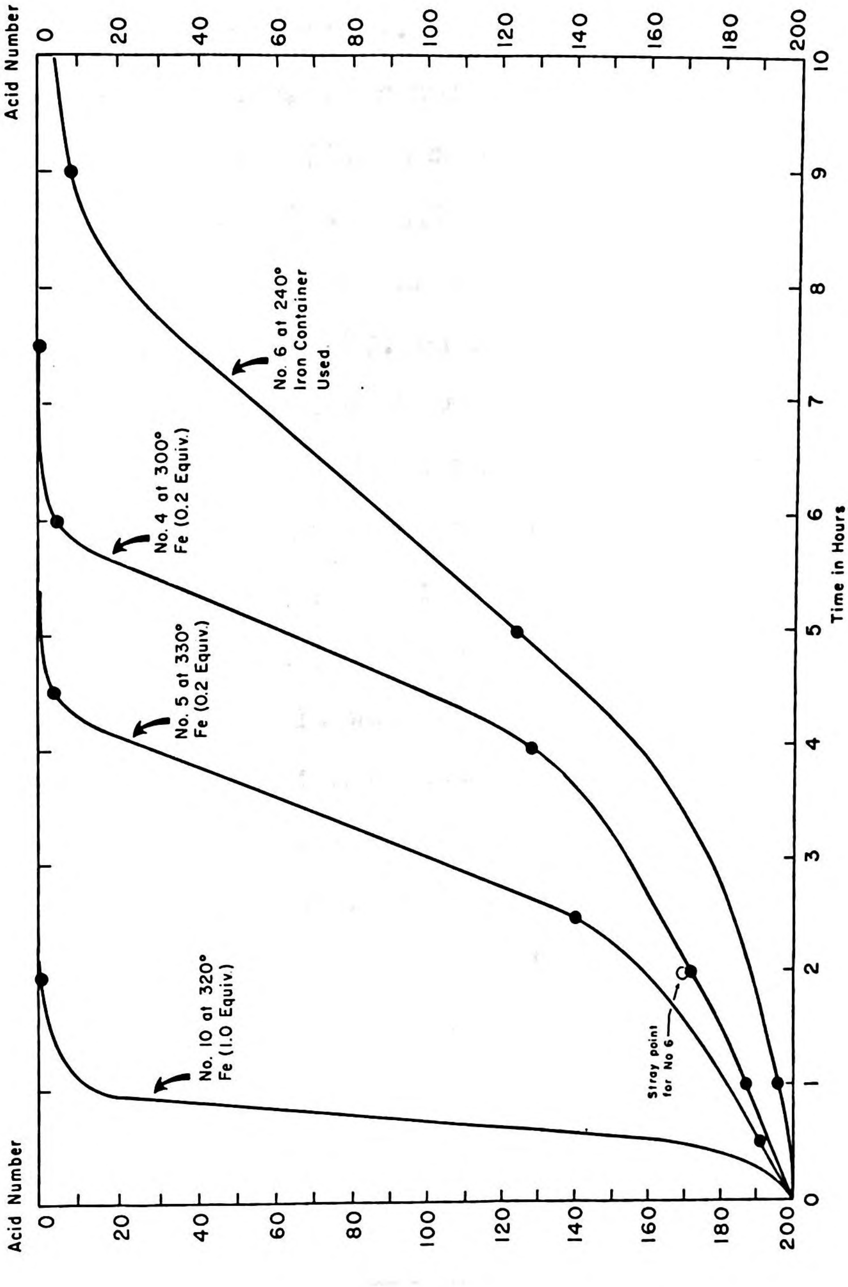
Acid Number
Acid Number
0
20
40
60
80
100
120
140
160
180
200
Time in Hours
0
1
2
3
4
5
6
7
8
9
10
No. 10 at 320°
Fe (1.0 Equiv.)
No. 5 at 330°
Fe (0.2 Equiv.)
No. 4 at 300°
Fe (0.2 Equiv.)
No. 6 at 240°
Iron Container
Used.
Stray point
for No 6

FIGURE I.

runs a product with a low acid number was obtained in 2 to 3 hours. However, a reaction temperature of 330°C. or higher is necessary. One run carried out at 310°C. required 20 hours to reduce the acid number to 3.3.

Fifty grams (0.176 moles) of pure stearic acid (Fisher, Reagent) and 5.0 grams (0.124 moles) of magnesium oxide (Coleman and Bell, U.S.P.) were heated for 2½ hours at 330°C. on the salt bath. Again, as the reaction was carried through the temperature range of 200° to 300°C. the fluid mixture became viscous, then less viscous at higher temperatures, but no frothing occurred. After heating for 2½ hours the mixture was cooled. The tan colored solid which formed had an acid number of 4.2. It was boiled with dilute sulfuric acid to remove magnesium oxide. It was boiled again with dilute sodium hydroxide to remove unreacted stearic acid. After drying it weighed 44.0 grams (0.087 moles- 91 per cent yield). The stearone was then recrystallized five times from ethyl alcohol. It appeared as very white, leaf-like crystals melting at 88° to 88.5°C.

A procedure suggested by Curtis[2] was followed in the preparation of stearone using magnesium oxide as a catalyst.

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[2] R. G. Curtis, et al., J. Soc. Chem. Ind. (London), 66, 402-7 (1947).

The magnesium oxide was heated to the reaction temperature and the stearic acid added in small portions to prevent frothing. The results of reactions using this method were no better than those in which the total acid and catalyst are heated together. Reaction time was not shortened and the temperature required was not decreased. However, the ketone was slightly less colored and more easily purified.

## Preparation of Stearone Oxime

A method described by Kipping[3] was used to prepare stearone oxime.

An ethyl alcohol solution of .42 g. (0.00083 mole) of stearone (M.P. 88.0°C.) was placed in a 50-ml. flask. To this was added a solution of .19 g. (0.00027 mole) of hydroxylamine hydrochloride (Baker and Adamson, Reagent) and .31 g. (0.0055 mole) of potassium hydroxide (Baker and Adamson, Reagent) in ethyl alcohol. The resulting solution was refluxed for 3 hours. The oxime was then precipitated out by cooling. It weighed .37 g. (0.00071 mole). Since the oxime is much less soluble in ethyl

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[3] F. S. Kipping, J. Chem. Soc., 57, 539 (1890).

alcohol than the stearone from which it was prepared it was purified by recrystallization from this solvent. It melted at 66° to 67°C., checking with literature values.

## Preparation of 18-Pentatriacontanol

Stearone was reduced to 18-pentatriacontanol by a method described by Easterfield[4] using sodium and n-amyl alcohol. The completion of the reduction reaction was checked by running an acetyl number on the product.

In a 500 ml. flask equipped with a reflux condenser were placed .8191 g. (0.0016 moles) of stearone (crude, M.P. 80° to 81°C.) and 170 ml. of n-amyl alcohol (Baker and Adamson, Reagent). The solution was refluxed for 10 hours. Seven grams of sodium metal was added during this time. A solid which separated upon cooling in an ice-salt bath weighed .6532 g. and melted at 84° to 86°C. An acetyl number (procedure outlined below) indicated that the stearone had been reduced almost completely to 18-pentatriacontanol. In all runs using stearone prepared from commercial stearic acid the alcohol melted at 86°C. or lower. The use of pure stearone (M.P. 88° to

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[4] T. H. Easterfield and C. M. Taylor, _J. Chem. Soc._, _99_, 2298-2300 (1911).

88.5°C.) in this reaction gave an alcohol which melted at 91.5° to 92°C. after several recrystallizations from ethyl alcohol. The alcohol is more soluble in ethyl alcohol than the stearone from which it was prepared.

The use of a method described by Bersin[5] in which a ketone is reduced to the corresponding alcohol by aluminum isopropoxide (the so-called "Meerwein-Ponndorf Reduction") proved to be of little value in the reduction of stearone. After 10 to 18 hours treatment by this method the acetyl number determination indicated less than 10 per cent conversion to the alcohol.

The 18-pentatriacontanol in the pure form is a white wax-like solid. When viewed under a magnifying glass the crystals appear much more granular than the stearone from which it was prepared.

## Preparation of the Acetate Ester of 18-Pentatriacontanol

18-Pentatriacontanol was acetylated by the general method using a large excess of acetic anhydride. 1.6964 g. (0.0033 mole) of 18-pentatriacontanol (M.P. 89°C.) and

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[5] T. Bersin, "Newer Methods of Preparative Organic Chemistry," p. 134.

approximately 50 ml. of acetic anhydride (Baker and Adamson, Reagent) were refluxed in a 100 ml. flask for 4 hours. Upon cooling, a solid acetate precipitated which weighed 1.8422 g. (.0033 mole) (slightly more than 100 per cent yield). The ester was separated from any unreacted 18-pentatriacontanol present by extraction with warm ethyl alcohol, in which the ester is insoluble. A saponification number was run using approximately 0.1 N alcoholic potassium hydroxide. An excess of the base was added and refluxed for 4 hours. The excess base was then titrated with approximately 0.1 N alcoholic hydrochloric acid. A saponification number of 101.7 was obtained (calculated saponification number is 101.9). After two recrystallizations from ethyl acetate and two recrystallizations from acetic anhydride, the acetate ester melted at 58° to 59°C.

The acetate ester of 18-pentatriacontanol from crude stearone (prepared from commercial stearic acid) always melted at 44°C. or lower, even after many recrystallizations.

## Preparation of Di-18-pentatriacontyl Oxalate

Initial plans for this research included the preparation of the 18-pentatriacontanol ester of oxalic acid by two or more methods.

Direct esterification using tin as a catalyst was attempted first. Reaction time and temperature were varied in different runs. In one run using crude 18-pentatriacontanol (M.P. 84° to 86°C.) a compound which was insoluble in ethyl alcohol and melted at 43° to 44°C. was obtained. In subsequent runs apparently no esterification occurred and the above work could not be duplicated.

The acyl halide method was used to prepare di-18-pentatriacontyl oxalate ($C_{72}H_{142}O_4$). The fact that the melting point of 18-pentatriacontanol is much higher than the boiling point of oxalyl chloride and the physical state of 18-pentatriacontanol is such that it is not easily attacked by the chloride caused some difficulty in arranging the proper reaction conditions. The 18-pentatriacontanol had to be used in the solid state, and this necessitated the use of a large excess of oxalyl chloride. This excess facilitated the formation of the mono-ester instead of the desired di-ester.

In order to get the solid 18-pentatriacontanol in the most easily attacked form, it was recrystallized slowly from a large amount of ethyl alcohol forming a fluffy precipitate. The ethyl alcohol was removed from the 18-pentatriacontanol by heating it at 45°C. for 16 hours in a vacuum oven.

Oxalyl chloride was prepared from previously dehydrated oxalic acid.

The oxalic acid was dried according to a method by Clarke in "Organic Synthesis,"[6] with some modifications. Benzene was used instead of carbon tetrachloride and the benzene which distilled was dried over calcium chloride and then returned to the distillation flask periodically. An ordinary side arm distilling flask and water condenser were used. The distillate was collected in a distilling trap which measured the amount of water driven off.

In a 1000-ml. distilling flask equipped with a stirrer were added approximately 400 ml. of benzene and 126 g. (1 mole) of oxalic acid (Baker and Adamson, Reagent). The mixture was distilled, with periodic additions of benzene, for 12 hours. At this time the benzene being distilled was clear, indicating that no water remained in the acid. The benzene was distilled

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6. A. H. Blatt, "Organic Synthesis," (Collective Volume III), p. 421.

off and the anhydrous oxalic acid dried for a short time in an oven at 100°C. to remove the remaining benzene.

Oxalyl chloride was prepared by the method of Staudinger[7] as presented in "Preparation of Organic Intermediates."[8] To a flask equipped with a calcium chloride tube were added 45 g. (0.5 mole) of anhydrous oxalic acid and 200 g. of phosphorous pentachloride (Baker and Adamson, Reagent). The flask was allowed to stand overnight after thoroughly mixing the two solids. A liquid formed on standing which was distilled. The fraction boiling from 60° to 70°C. was collected and redistilled. The fraction at 63° to 64°C. was collected. Fifteen millileters of the chloride was collected (35.4 per cent yield).

In a large test tube equipped with a calcium chloride tube, were placed 2.6401 g. (0.0052 moles) of pentatriacontanol and an excess of oxalyl chloride. This was allowed to stand for two hours at room temperature and then for two hours in a water bath at 100°C.

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[7] H. Staudinger, <u>Ber</u>., <u>41</u>, 3563 (1908).

[8] D. A. Shirley, "Preparation of Organic Intermediates," pp. 242-3.

The remaining oxalyl chloride was converted to oxalic acid by heating the mixture with water. The solid which separated upon cooling was dissolved in petroleum ether (Baker and Adamson, Reagent) and neutralized with dilute alcoholic potassium hydroxide. The acid salts and incompletely esterified materials were removed by a method of Hönig and Spitz[9] in which the petroleum ether solution is extracted twice with a fifty per cent alcohol-water solution. The petroleum ether was evaporated, depositing the di-ester which weighed .3807 g. (0.00036 moles, 13.8 per cent yield). A saponification number of 105.7 (calculated 104.9) was obtained using dilute alcoholic potassium hydroxide. The ester melted at 56° to 57°C. after three recrystallizations from ether. It was a rather hard wax-like solid which was soluble in ether and chloroform, but was not soluble in ethyl alcohol. Since boiling the ester with ethyl alcohol causes it to dissolve, it must undergo alcoholysis to form 18-pentatriacontanol and ethyl oxalate which are both soluble in ethyl alcohol.

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[9] M. Hönig and G. Spitz, Z. angew. Chem., 4, 565 (1891).

The ester prepared in another run using oxalyl chloride was extracted in a Soxhlet extractor. The crude material melted at 49° to 53°C. and had a saponification number of 106.0. The yield was so small that it did not permit extensive purification.

A chloroform solution of 18-pentatriacontanol and oxalyl chloride was vigorously stirred for 10 hours under a nitrogen atmosphere. No apparent reaction took place and the solid recovered was the alcohol.

## IV

## DISCUSSION OF EXPERIMENTAL RESULTS

Both magnesium oxide and iron were found to give excellent yields of stearone in the ketonization of stearic acid. In carrying out this reaction we encountered excessive frothing as did all previous investigators.

Frothing was shown by Curtis[1] and co-workers to be related to the rate of liberation of carbon dioxide. They suggested a mechanism for the reaction and attempted to connect the occurrence of frothing with this mechanism. Frothing was considered to arise from a change in rate of evolution of carbon dioxide which in turn was connected to a mechanism which included keto-acid and keto-acid salt formation. According to their theory, as long as the acid was in excess, a slow rate of liberation of carbon dioxide resulted from the formation and decomposition of a keto-acid and keto-acid salt. When the catalyst became in excess a faster rate occurred from the decomposition of a metal soap.

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[1] R. G. Curtis, et al., J. Soc. Chem. Ind. (London) 66, 402-407, (1947).

They used a method of preparation in which the catalyst was kept in excess by adding the acid in portions. This, therefore, prevented a change in the rate of liberation of carbon dioxide. No frothing resulted.

The mechanism proposed by Curtis does not account for the fact that frothing occurred when the total amount of acid and catalyst were heated together in a container, even when excess catalyst was used. Another fact not accounted for is that iron always caused frothing, even when excess iron was heated to the reaction temperature and the acid added portion-wise.

In our experiments, we observed that if the temperature of the reaction mixture is increased slowly the mixture becomes viscous at about 250°C., then more viscous as the temperature is increased. When a temperature of 310°C. to 320°C. is reached the mixture suddenly becomes much less viscous. This viscosity at lower temperature may be the result of an accumulation of metal soap which could trap the carbon dioxide. This accumulation of carbon dioxide and sudden release as the viscosity decreases may be the cause of troublesome frothing.

By increasing the stirring rate as the viscosity of the reaction mixture increased, sudden frothing was almost entirely avoided. This increased rate of stirring allowed the entraped carbon dioxide to escape. This physical method of accounting for frothing would also account for the fact that Curtis always got frothing with iron. Possibly iron soap is more viscous than others.

Frothing was further diminished by a rapid increase in the temperature of the reaction mixture over the range of high viscosity. By combining this with rapid stirring we were able to carry out the reaction using iron or magnesium oxide as the catalyst with little or no frothing.

For the preparation of large quantities of ketone and for products not requiring a high degree of purity, evidence in the runs made in this laboratory indicated that iron is the best catalyst. Reactions utilizing iron were found to give a product with a low acid number in a shorter period of time and at a lower temperature than those in which magnesium oxide was used. However, the product was more difficult to purify. In small laboratory preparations where time and temperature are not major considerations, the use of magnesium oxide is considered superior. A pure compound was prepared easier by this method.

A number of experiments were run to determine if frothing and foaming could be prevented by the addition of anti-foam agents. Heavy metal soaps, silicones, and other anti-foam agents had little or no effect.

In order to prepare pure stearone one must use pure stearic acid as the starting material. The best commercial grades produce mixtures which are extremely difficult to separate by all known procedures. Starting with pure stearic acid, we prepared pure stearone melting at 88.0°C. to 88.5°C. Its oxime derivative melted at 66°C. to 67°C. These values agree with those reported in the literature.

Reduction of stearone to 18-pentatriacontanol by the use of sodium and amyl alcohol was superior to reduction using aluminum isopropoxide and isopropyl alcohol. The acetyl number and melting point of the 18-pentatriacontanol checked with literature values. Its acetate derivative melted as reported and its saponification number agreed with the theoretical value.

The 18-pentatriacontanol ester of oxalic acid was prepared in greatest yield by the action of oxalyl chloride on the alcohol.

One preparation was made using 18-pentatriacontanol and anhydrous oxalic acid. Negative results were obtained when ethyl oxalate was heated with the acetate ester of 18-pentatriacontanol. This reaction deserves much more extensive study.

A saponification number agreeing with theory and a constant melting point after several recrystallizations were taken as sufficient evidence that the compound prepared was di-18-pentatriacontyl oxalate. Time did not permit the isolation and characterization of the mono-ester.

# V

## SUMMARY

(1) Ketonization of stearic acid using iron and magnesium oxide was studied. Some previously unobserved facts were noted. These facts suggested a simple theory to account for troublesome frothing encountered by all investigators. On the basis of this theory a trouble free method of ketonization giving yields better than 90 per cent was worked out. Physical constants of stearone and its derivatives were determined and found to agree with literature values.

(2) The reduction of stearone to the corresponding alcohol, 18-pentatriacontanol was carried out by two methods. The sodium-amyl alcohol method was found superior to the aluminum isopropoxide method for this reduction. Physical constants and derivatives of this alcohol checked with literature values. Acetyl number determinations were used to check the extent of reduction of the ketone by each method.

(3) A new compound, di-18-pentatriacontyl oxalate, was prepared. A constant melting point after several recrystallizations and a saponification number agreeing with theory were taken as conclusive evidence that the compound had been prepared.

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(Thesis Approval Form)

Name of Candidate **Edward Albert Cress**

Major Subject KETONIZATION OF STEARIC ACID AND THE

Title of Thesis PREPARATION OF DI-18-PENTATRIACONTYL OXALATE

Approved by:

Thesis Committee:

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Dean of the Graduate School

Date Sept. 14, 1956