

III. CONSTITUTION OF LUBRICATING OILS

Dr. A. Schaafsma

Frames 2806-2810

Translation

2806

GENERAL

March, 1942

III-1

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The research group to which this investigation was assigned began work in the month of March, 1942. It was first necessary to plan and determine upon a schedule for the investigation, by which it could best be accomplished. For this we first contacted various experts in the field of lubricating oil research in the laboratory in Amsterdam. In addition, conferences were held with several gentlemen of the test station (Test Station, Delft) of the B.P.M., where they are especially conversant with all the practical problems relating to lubrication.

The data obtained in this way were compared, and on the basis of these data, a preliminary program for the investigation was drawn up.

Finally, consideration was given as to how the parts of this program might best be accomplished within the limits of the research group concerned, and in what sequence the different component parts should be started.

We will discuss more carefully in the next monthly report the final program for the plan of experimental work, investigation of several parts of which has already been started in the meantime.

April, 1942

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In connection with the preliminary discussions, the account of which was given in our monthly report for March, we can now discuss the program for the experimental work more carefully, since we have started this program.

First one might ask what result we could really expect from an exhaustive investigation concerning the constitution of lubricating oils. The answer to this was that it was hoped to determine which type of molecules possesses especially favorable properties for purposes of lubrication.

The next step would then be either to separate these desired types of molecules from crude petroleum or to synthesize them in order to be able to make practical use of the knowledge gained and to obtain better results. However, such special products will always be commensurately more expensive and, therefore, it is concluded that only definite fields of application can be considered, in which a need already exists for a better lubricant, and which means a proportionately limited market.

We have critically examined the various fields of application of lubricating oil with the gentlemen of the Test Station, Delft and from this have come to the conclusion that lubricating oil for gasoline motors (especially aircraft motors), hot steam cylinder and large Diesel motors should constitute by far the most important subject for our research.

It can now be asked, which are the most important demands which will be placed upon the lubricant in these uses, in order to conclude therefrom which properties should be considered for examination in our investigation. It is then found that the following points are of real significance:

1. commensurately lower pour point
2. flat temperature-viscosity curve
3. low volatility (i.e., in the first approximation, as high a molecular weight as possible at a given viscosity)
4. high oxidation stability; desirable flow behavior of the oxidation product; sludge supporting action
5. slight corrosion of lead bronze and iron
6. good wetting of metal surfaces.

As the next step, therefore, procedures now had to be devised for measuring these various properties; before this, however, it would be desirable to think about what kinds of substances would be the subject of the investigation, since in this choice, certain inferences have already been included concerning the measuring procedures to be developed.

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The substances which we intended to investigate can be arranged in four groups:

- I. Technical lubricating oils of quality known from the art, investigation of which would serve in a certain degree to evaluate our measuring procedure in correlation with practice.
- II. Certain constituents of natural lubricating oil, which have been prepared from it by various processes (such, for example, as those devised by Rhenania, namely chromatographic separation\* distillation, and extraction.)
- III. Pure hydrocarbons of various types and exactly known structure. The investigation of these substances was likely to yield considerable information concerning the influence of the molecular type upon the lubricating action.
- IV. Synthetic products, of which, to be sure, it can not be said that the molecular type is accurately known in all respects, but of which, however, the general characteristics of the molecular species are established on the basis of the synthesis procedure.

It is clear that the third group, which, however, is extremely

\* Translator's note: Probably percolation through silica gel, activated alumina, or the like, wherein certain color bands appear along the bed as the result of preferential adsorption of certain components of the lubricating oil. They probably have a refining or separation process based upon this preferential adsorption and subsequent desorption.

important for the object of the investigation, requires a considerable limitation of the measuring procedure to be selected. The pure high molecular weight hydrocarbons are always available only in very limited quantities, and, therefore, the measuring procedures for the six points named above should be planned in such a way that they can be performed with very small quantities of oil; procedures which are to a certain degree semi-micro in nature should be developed.

If we now make a survey of the parts of the investigation which should be undertaken first, particularly because they will require a proportionately long time for development, we find that the synthesis of the pure hydrocarbons (III) and the development of the measuring procedures for temperature-viscosity behavior (2), oxidation stability (4), corrosion (5), and wetting of metal surfaces (6) must be considered first.

Accordingly, various gentlemen have already been entrusted with III-4  
2310  
carrying out this part of the work and have already started with it, namely, Dr. Verberg with the hydrocarbon synthesis, Dr. Nederbragt with the viscosity study, and Mr. van der Tijden with the investigation relating to oxidation stability, corrosion, and wetting of metal surfaces.

Obviously we will also gradually attack the other points and seek to carry out the development of the entire investigation as vigorously as possible.

III. CONSTITUTION OF LUBRICATING OILS

Dr. G. Verberg

Names

2011-12

2019-23

2012-53

2016-58

2014-67

2017-73

2014-95

2013-15

2012-23

2011-54

2016-67

QualificationSYNTHESIS OF PURE HYDROCARBONS

NY-5

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INTRODUCTION

In the selection of the pure hydrocarbons to be synthesized, from the standpoint of the entire investigation, one can proceed in two entirely different ways.

a. One can proceed from our knowledge of natural lubricating oils, from which it appears that one has to deal with a very complicated mixture, but on the basis of data from analyses for cyclics, it can be stated that definite structural elements are present (more or less branched hydrocarbon chains of different lengths, aromatic and naphthenic ring systems).

To be sure, we do not know how these elements are put together in the molecules actually present, but on the other hand, we well know the magnitude of the average molecular weight.

One can now set as the goal the synthesis of definite characteristic molecules of the correct molecular weight, in which the structural elements are put together in exactly known different ways.

b. In case one has an idea of favorable molecular types for purposes of lubrication on the basis of my considerations which relate to lubrication, one can seek to produce those types directly by synthesis.

For the present, we will proceed in the manner first described; however, we will not disregard the second method in doing so. Thus, for

example, without further ado, we will eliminate those kinds of molecules, concerning which it is known from experience that they have less favorable properties, such, for example, as very highly branched aliphatics and highly aromatic products. In general, we will limit ourselves at first to more or less elongated molecules.

In order then to limit oneself to the still extremely large number of conceivable possibilities for synthesis, it is well to consider the following:

1. We must produce substances, the structure of which, wherever possible, is known for certain and which are ordinarily really pure.
2. Preferably we must produce about 100-200 g of each preparation.
3. It would obviously be desirable, for purposes of comparison, to select the various preparations in such a way that all of them would have an equally large number of carbon atoms per molecule.

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These three requirements have a very powerful limiting effect, since at present, only those synthesis methods are considered, for which the structure of the resulting product is unambiguously established, and which do not give too small a yield. In addition, in the synthesis of high molecular weight products, it was decided to start out with basic substances with not too low a molecular weight. However, these starting materials should then either be available in the pure state, or it should be possible to purify them fairly well. The already limited number of commercial products available, which are satisfactory for this purpose, may become considerably more limited still owing to the present state of affairs.

On the basis of an exhaustive study of the literature, in which the considerations just mentioned were taken into account, we concluded that it would be the most favorable to select the number of carbon atoms in the hydrocarbons at 36 and to seek to prepare the following C<sub>36</sub> hydrocarbons:

- one aliphatic hydrocarbon with a straight carbon chain
- two aliphatic hydrocarbons with branched carbon chains and very different degrees of branching
- two mixed aliphatic-aromatic hydrocarbons with one ring or two rings
- two mixed aliphatic-hydroaromatic hydrocarbons with one ring or two rings.

During the past month, we were busy with the procurement and preparation or purification of the starting materials required for these syntheses. In the report for next month, we hope to be able to discuss more intimately the synthesis methods which we plan to use, since we will then know what possibility there is of obtaining certain starting products.

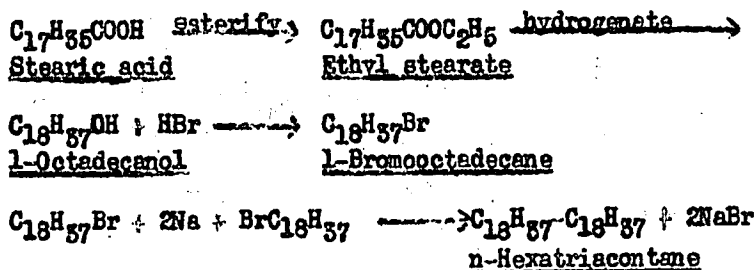
May, 1942

III-12  
2819INTRODUCTION

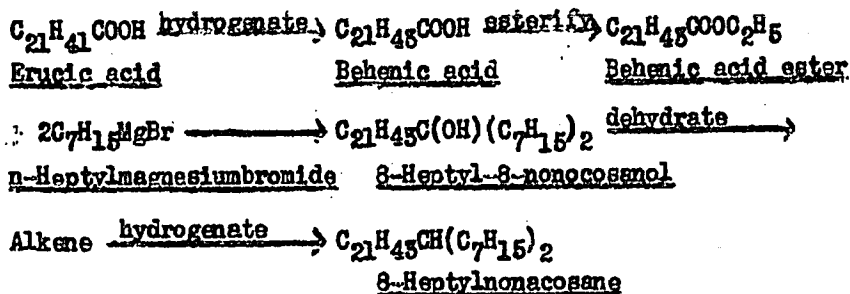
In view of the requirements described in our preceding monthly report (April, III 5-6), which must determine which hydrocarbons are suitable for the lubricating oil investigation, we have, after study of the literature, set up one preliminary plan of work - in accordance with the classification indicated on page III-6. In this, we have previously only considered aliphatic compounds and compounds with rings containing six carbon atoms, since the literature indicated that the data relating to the preparation of hydrocarbons with rings containing five carbon atoms or with complicated ring systems are scarce and not always reliable.

The preliminary program includes the following compounds:

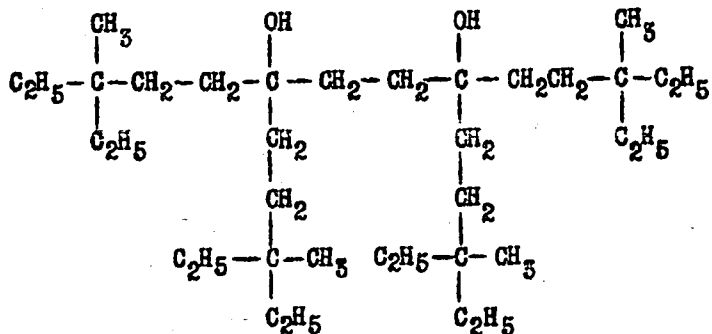
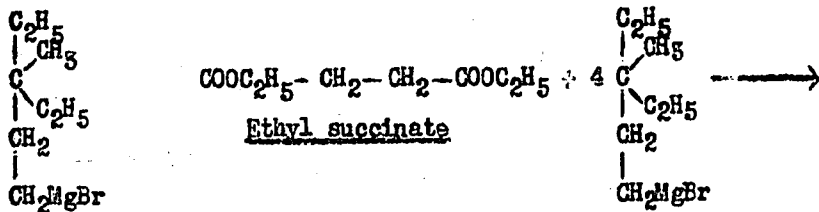
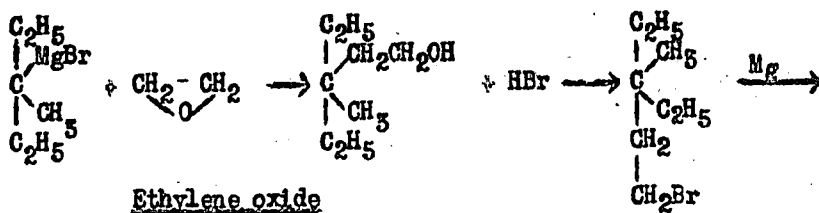
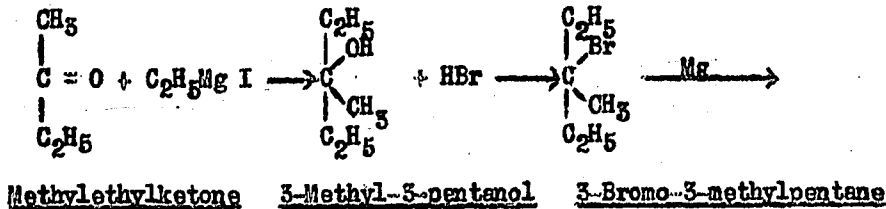
- I. Preparation of an unbranched aliphatic hydrocarbon  $C_{36}H_{74}$  (n-hexatriacontane).

Reaction scheme:

- II. Preparation of a branched aliphatic hydrocarbon with one long side chain: 8-n-heptylnonacosane,  $C_{21}H_{43}CH(C_7H_{15})_2$ .

Reaction scheme:III-15  
2820

## III. Preparation of a highly branched aliphatic hydrocarbon.

Reaction scheme:

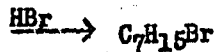
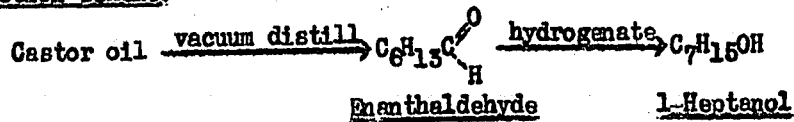
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Dehydrate this diol and hydrogenate the diolefin obtained thereby to the saturated hydrocarbon.

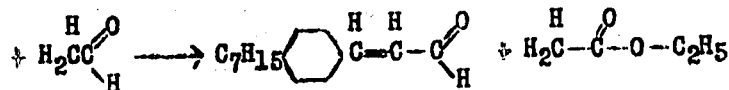
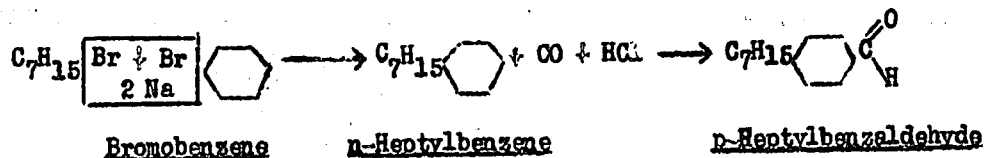
We have selected this hydrocarbon as being representative of an extremely branched type; however, at present we do not intend to synthesize such a molecule, which probably has few properties favorable for lubrication.

IV. Preparation of a mixed aliphatic-aromatic hydrocarbon with two benzene nuclei in the molecule.

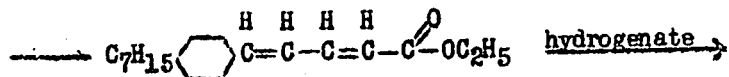
Reaction scheme:



1-Bromoheptane



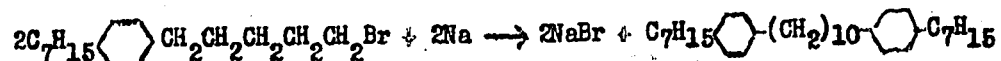
Acetaldehyde    3-(p-Heptylphenyl)acrolein    Ethyl Acetate



1-(p-Heptylphenyl)-4-carboethoxy-1,3-butadiene



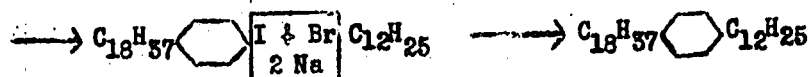
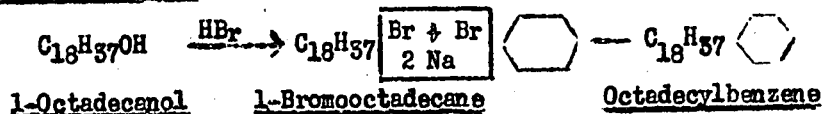
5-(p-Heptylphenyl)-1-pentanol                      5-(p-Heptylphenyl)-1-bromopentane



1,10-Di(p-heptylphenyl)decane

V. Preparation of a mixed aliphatic-aromatic hydrocarbon with one benzene nucleus in the molecule: p-Octadecyldecylbenzene.

Reaction scheme:



p-Iodoctadecylbenzene    1-Bromododecane                      p-Octadecyldecylbenzene



- VI. Preparation of a mixed aliphatic-hydroaromatic hydrocarbon with two cyclohexane nuclei in the molecule. 1, 10-Di(p-heptyl-cyclohexyl)decane.

This compound can be prepared from the final compound in number IV by hydrogenation of the benzene nuclei.

- VII. Preparation of a mixed aliphatic-hydroaromatic hydrocarbon with one cyclohexane nucleus in the molecule. p-Octadecyl-dodecylcyclohexane.

This compound can be prepared from the final compound in number V by hydrogenation.

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2322

### SUMMARY OF THE INVESTIGATION

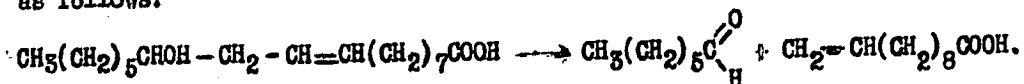
#### 1. Preparation of Stearic Acid.

For the preparation of  $C_{18}$  alcohol, which is not available as starting material for synthesis of the various hydrocarbons mentioned in the program cited above, we have commenced with the preparation of pure stearic acid, and have proceeded with this preparation from a technical mixture of palmitic acid and stearic acid, which was rich in oleic acid. This mixture was subjected with good success to a hydrogenation for conversion of the oleic acid into stearic acid.

The fractionation of the palmitic-stearic acid mixture is now in progress.

#### 2. Preparation of Enanthaldehyde.

As the starting product for the preparation of mixed aliphatic-aromatic hydrocarbons, in which two benzene nuclei are present in the molecule (see above under IV), we have found enanthaldehyde essential. This material results from the vacuum distillation of castor oil, which contains as its principal constituent the glyceride of ricinoleic acid; in this way, a mixture of enanthaldehyde (heptanal) and 10-hendecenoic acid is obtained as follows:



The distillation, which proceeds with violent foaming of the contents of the distillation flask, should be terminated after some time, since a rather sudden polymerization sets in. The contents of the distillation flask are thereby changed into a solid, spongy, sticky mass, which can be removed from it only with difficulty. Although the polymerization commences rather suddenly, we determined after several distillations that, immediately before its appearance, the foam becomes viscous. It is recommended that the distillation be stopped at this instant, when the contents, which have not yet cooled, can still be removed from the flask fairly easily.

The distillate obtained was then vacuum distilled in order to separate the enanthaldehyde from the 10-hendecenoic acid; after that the enanthaldehyde which distilled over was redistilled. The product obtained had a boiling point of 51 C at 15 mm Hg and a  $n_D^{20} = 1.4120$ .

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The amount of distillate (enanthaldehyde and 10-hendecenoic acid) obtained in the vacuum distillation of castor oil amounts to about forty per cent of the starting material as a result of the polymerization which occurs. The yield of enanthaldehyde accordingly is also low (in a number of experiments, only 828 g of enanthaldehyde, equal to 16 per cent, was obtained from 5 kg of castor oil). In the distillations, we have always raised the temperature as high as possible, because it is known from the literature that the yield is better the higher the temperature which is chosen.

Enanthaldehyde was converted into 1-heptanol as has already been described (see page I B 20 of this report). We will convert this further to 1-bromoheptane.

October - November, 1942

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#### PREPARATION OF STEARIC ACID

As was already mentioned in the May report (page III-15), we have hydrogenated a technical mixture of palmitic acid and stearic acid which was rich in oleic acid for conversion of the oleic acid into stearic acid. This hydrogenation was carried out at a pressure of 186 atmospheres with nickel-on-kieselguhr as the catalyst, while, in order to prevent the conversion of the nickel in the catalyst into a nickel soap to as great an extent as possible, the hydrogenation temperature was kept as low as possible (100 C). We sought to prevent the conversion into nickel soap, because we were afraid that its presence in the fractionation of the palmitic acid-stearic acid mixture could produce cracking. In order to obtain a mixture as free of nickel as possible, we first converted the hydrogenated mixture into the corresponding sodium salts and separated the nickel hydroxide formed by filtration.

After the liberation of the fatty acids, decomposition occurred during their fractionation, which increased as the fractionation progressed. A number of fractions were obtained which were much less pure than the palmitic acid-stearic acid fractions, which we had obtained in the fractionation of the unhydrogenated mixture. Therefore, we decided to fractionate without the preceding hydrogenation in the future. In addition, it appeared to us to be desirable to first convert the fatty acids into their methyl esters, since the fractionation of these esters, which have lower melting points than the acids themselves, can be carried out more easily.

By esterification of the starting product, which is rich in oleic acid, with methyl alcohol, a mixture was obtained which consisted of a solid and a liquid part. Since we supposed that the oleic acid ester was concentrated principally in the liquid part, we have drawn off this part and fractionated

the solid part. As is evident from the following table, these solid constituents consist of palmitic acid ester to a great extent, and the quantity of stearic acid ester is much less; in addition, there is a considerable intermediate fraction concerning the composition of which we are not certain.

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Starting material,	2830 g = 3150 ml		
First light oil	: 100 ml	Freezing point :	low
Palmitic acid ester fraction	: 1600 ml	" "	: 28-29 C
Intermediate fraction	: 500 ml	" "	: low
Stearic acid ester fraction	: 800 ml	" "	: 35-36.7 C
Higher boiling oil	: 100 ml	" "	: low
Kettle residue	: 150 ml		

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After saponification, the acid was extracted from the palmitic acid ester fraction with sufficient purity that it needed to be recrystallized from methylethylketone only once (melting point, 62.2-62.5 C; the literature\* mentions a melting point of 62.6 C). From the stearic acid ester fraction, the pure acid was also extracted with commensurately less trouble, since after saponification of the ester, the potassium salt was recrystallized twice from 50 per cent alcohol\*\* and afterward the free acid was recrystallized twice from methylethylketone (melting point, 69.2-69.4 C; the literature\* mentions a melting point of 69.3 C).

#### CONCLUSIONS

By fractionation of a mixture of palmitic acid and stearic acid, obtained by hydrogenation of a mixture of palmitic acid and stearic acid which is rich in oleic acid, using nickel as the catalyst, very impure products were obtained - probably caused by catalytic decomposition resulting from the presence of traces of nickel which had not been completely removed.

Palmitic acid and stearic acid could be prepared in the pure state by fractionation of a mixture of the methyl esters of a mixture of palmitic acid and stearic acid which is rich in oleic acid, with subsequent saponification of the ester fractions and recrystallization of the acids which were liberated.

#### PLANNED ADDITIONAL RESEARCH

We will convert a part of the pure stearic acid which we have prepared into the corresponding alcohol; from another part of it we will prepare stearates.

\* ) De Visser, Rec. trav. chim., 17, 186, 347 (1898).

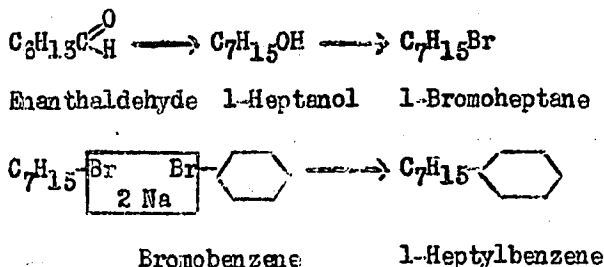
\*\* ) Separation of palmitic acid from stearic acid according to Scheringa, Chem. Weekblad., 29, 605 (1932).

December, 1942

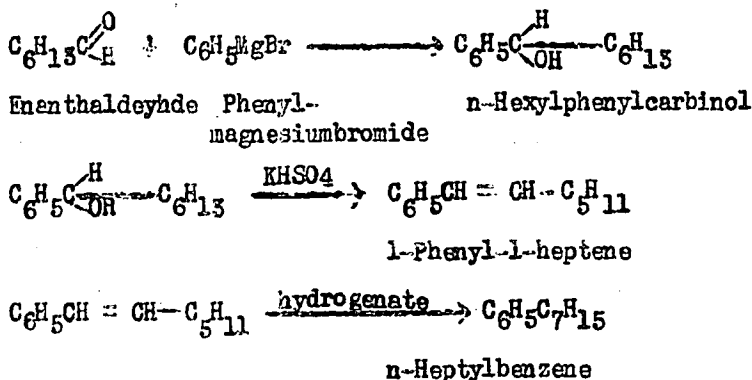
III-44  
2856PREPARATION OF 1,10-DI(p-HEPTYLPHENYL)DECANEINTRODUCTION

In the preliminary plan under Number IV in the May report, 1,10-di(p-heptylphenyl)decane was discussed. As the first step for its preparation, as was already mentioned in the report specified, the preparation of enanthaldehyde was encountered.

The first part of the reaction scheme for the preparation of hydrocarbon No. IV reads as follows:



Since the literature indicated that the last step, namely the reaction of 1-bromoheptane with bromobenzene, would give a poor yield, we decided to proceed as follows:

SUMMARY OF THE INVESTIGATION

We have prepared n-hexylphenylcarbinol as the first step in the synthesis of n-heptylbenzene. In the preparation of this material, which is not described in the literature, we proceeded from the basic thought that aldehydes can be reacted with Grignard compounds, with the formation

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of secondary alcohols. For this purpose, we have converted a solution of bromobenzene in absolute ether into phenylmagnesiumbromide according to the Grignard procedure. After completion of the reaction, a solution of enanthaldehyde in ether was admixed with continuous ice cooling; afterward, it was boiled for 15 minutes, cooled again in ice, and some finely crushed ice was added to the reaction mixture. Then 1:1 hydrochloric acid was added and after cooling and stirring, the water and ether layers were separated. The aqueous layer was extracted three times with ether and the combined ether extracts were washed with water and treated with concentrated bisulfite solution for removal of the unconverted enanthaldehyde. After drying over sodium sulfate, the ether was distilled off and the n-hexylphenylcarbinol was vacuum distilled. The product obtained, with a yield of 85 per cent, had a boiling point of 160 C at 19 mm Hg.

For splitting water out of the n-hexylphenylcarbinol for the preparation of 1-phenyl-1-heptene, which material likewise has not been described in the literature, we have made use of the general rule that secondary alcohols can split out a molecule of water under the influence of  $\text{KHSO}_4$  and thereby be converted into the corresponding unsaturated compound. For this purpose, we have heated n-hexylphenylcarbinol with anhydrous  $\text{KHSO}_4$  at 180 C in vacuum for half an hour, so that the 1-phenyl-1-heptene formed distilled over. After the greater part of the reaction product had distilled over, the reaction gradually proceeded more and more slowly. For this reason, the experiment was interrupted for an instant and some more anhydrous  $\text{KHSO}_4$  was added. Then the reaction proceeded smoothly to the end of the experiment. The distillate consisted of a system of two layers, namely, a layer of 1-phenyl-1-heptene and a layer of water. The latter was withdrawn, and after that, the hydrocarbon layer was shaken with sodium carbonate solution in order to remove the  $\text{SO}_2$  present. After drying over sodium sulfate, the 1-phenyl-1-heptene was vacuum distilled twice.

The yield is nearly quantitative. The compound smells like ionone.

The hydrogenation of the 1-phenyl-1-heptene to 1-phenylheptane was carried out according to the general principle that unsaturated compounds react with hydrogen at room temperature under the influence of platinum. In order to prevent the hydrogenation of the benzene nucleus, the platinum catalyst was alloyed with a trace of iron, according to Weygand and Werner\*). However, the hydrogenation, which proceeded smoothly at first, slowed up toward the end of the experiment; the reaction could no longer be started again in the usual manner by churning the catalyst with air. Since the 1-phenylheptane preparation, which was obtained with good yield, still contained a noticeable amount of 1-phenyl-1-heptene, we removed the latter by shaking with 80 per cent of (1:1) sulfuric acid. The product obtained, after being washed with water and sodium carbonate solution, dried with calcium chloride, and fractionated, had a boiling point of 104 C (10 mm Hg, not corrected) and a  $n_D^{20}$  of 1.4865. The literature \*\*) reports a boiling point of 116-118 C (12 mm Hg) and a  $n_D^{20}$  of 1.4860 or 1.4865.

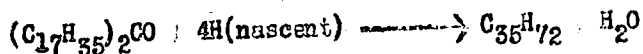
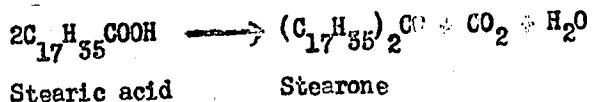
\*) Ber., 71, 2469 (1938).

\*\*) Ber., 45, 2179 (1912); Ber., 72, 1893 (1939).

PREPARATION OF n-PENTATRIACONTANE, C<sub>35</sub>H<sub>72</sub>III-46  
2858INTRODUCTION

Since it is probable that considerable time will elapse before the unbranched paraffin, C<sub>36</sub>H<sub>74</sub>, is ready, we decided to prepare the unbranched paraffin, C<sub>35</sub>H<sub>72</sub>, next, since the preparation of this hydrocarbon probably requires less time. Then lubricating oil tests will be carried out with this hydrocarbon while waiting for the hydrocarbons being synthesized in accordance with the preliminary program.

We intend to undertake the preparation in accordance with the following scheme:

SUMMARY OF THE INVESTIGATIONPREPARATION OF STEARONE

The conversion of stearic acid into stearone follows the procedure described by Grün \*), Easterfield \*\*), and Backer and Strating \*\*\*), in which 240 g of stearic acid, mixed with 24 g of iron turnings, was heated to 300 C in a metal bath. After completion of the reaction, which is apparent when the evolution of carbon dioxide ceases, the reaction product was extracted in an extraction thimble with petroleum ether. After the iron present had been removed in this way, the petroleum ether was distilled off, and the product obtained was heated for some time on the steam bath with concentrated sodium hydroxide solution for conversion of the stearic acid present into the corresponding sodium salt. The supernatant stearone layer, which became solid after cooling, was subsequently washed with water, and was then heated for some time with hydrochloric acid in order to decompose the small amount of iron compounds present. After separation of the hydrochloric acid, the product was recrystallized several times from methylethylketone, to which a little decolorizing carbon had been added.

The melting point of the slightly impure stearone, which was very readily obtained with a good yield, was 87-88 C.

\*) Z. angew. Chem., 39, 421 (1926).

\*\*\*) J. Chem. Soc., 99, 2297 (1911).

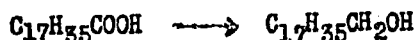
\*\*\*) Rec. trav. chim., 59, 934 (1940).

January, 1943

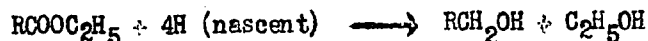
PREPARATION OF 1-OCTADECANOL FROM STEARIC ACIDIII-50  
2864INTRODUCTION

In the report for October - November, 1942, the separation of pure palmitic acid and stearic acid from a technical mixture of palmitic acid, stearic acid, and oleic acid was described.

The next step in the preparation of n-hexatriacontane consists of the preparation of 1-octadecanol from stearic acid:



The most usual method for the conversion of an acid into an alcohol with the same number of carbon atoms is the method of Bouveault and Blanc. In this method, the acid in the form of an ester is hydrogenated with nascent hydrogen:



The nascent hydrogen is obtained in this case by the reaction of sodium with alcohol.

However, the method of Bouveault and Blanc is very bothersome. Last year it was noted in the literature <sup>1)</sup> that the conversion of an acid into an alcohol with an equal number of carbon atoms can also be carried out according to the method of Adkins, in which an ester of the corresponding acid together with hydrogen, is heated in an autoclave in the presence of copper chromite catalyst.

Next we tested the method of Adkins. Since this appeared to be unsuccessful at first, the method of Bouveault and Blanc was subsequently used. The latter method was carried out readily and gave good yields. However, when we repeated the experiment afterwards, using the Adkins catalyst, but with a very pure ester, this procedure was also successful and produced a very good yield indeed.

Since our supply of stearic acid is limited and we have at our disposal an ample supply of palmitic acid, for which there is no use at present, we have thoroughly tested the method of Bouveault and Blanc as well as the method of Adkins with palmitic acid.

SUMMARY OF THE INVESTIGATIONPREPARATION OF THE ETHYL ESTERS OF PALMITIC AND STEARIC ACIDSIII-51  
2865

The preparation of the ethyl ester of palmitic or stearic acid was effected by dissolving pure palmitic or stearic acid in ethyl

1) Adkins and Folkers, J. Am. Chem. Soc., 53, 1095 (1931);  
Folkers and Adkins, J. Am. Chem. Soc., 54, 1145 (1932).

alcohol and adding strong sulfuric acid. This mixture was refluxed for five hours on the steam bath. During the heating, the ester formed separated from the originally clear liquid as a yellow upper layer. This layer, which was solid upon cooling, was separated and washed with alcohol.

CONVERSION OF THE ETHYL ESTERS OF PALMITIC- AND STEARIC ACIDS ACCORDING TO THE PROCEDURE OF BOUVEAULT AND BLANC

The original method of Bouveault and Blanc was carried out by adding pieces of sodium to a solution of the ester to be reduced, dissolved in absolute alcohol. The yields obtained with this procedure are often low. This results from the fact that, in addition to the hydrogenation, saponification of the ester also occurs. This is especially true if the alcohol is not entirely free of water. By the action of sodium upon the water present, sodium hydroxide is formed, which causes saponification of the ester. Obviously, the sodium used should be properly freed of incrustations of sodium hydroxide.

Besides the saponification which always occurs, the violence of the reaction is also very troublesome.

The method of Bouveault and Blanc has been considerably improved by Bleyberg and Ulrich <sup>1)</sup> by the use of butyl alcohol instead of ethyl alcohol. The sodium reacts with the butyl alcohol much less vigorously so that the hydrogen liberated is better utilized. However, since butyl alcohol was not available, we used isoamyl alcohol.

At first we carried out the hydrogenation with varying success, using the method of Bouveault and Blanc in the modified form of Bleyberg and Ulrich. One time we would obtain cetyl alcohol with fairly good yield; the next time, almost nothing. Finally, we found out how we could obtain good results. In order to do this, the reaction should be carried out at a temperature below the melting point of sodium. During the experiment, it is difficult to see if the sodium is molten because it is covered with a layer of alcoholate. The molten sodium has a small surface which, in addition, becomes covered with alcoholate so that little reaction can occur between the sodium and the alcohol. On this basis, it is necessary to place a thermometer in the flask. Therefore, care was taken that the temperature did not go above 80 C during the reduction.

After the reaction of the sodium with the amyl alcohol has stopped, 96 per cent alcohol is added, according to the method of Bleyberg and Ulrich, in order to dissolve the rest of the sodium, which is used in great excess (about 300 per cent excess). However, we have used absolute alcohol in order to prevent the eventual saponification of the still unhydrogenated ester, and in order to hydrogenate the latter.

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1) Ber., 64, 2504 (1931).



In this way a clear, somewhat yellow colored solution resulted, which separated into two layers with the addition of water. The upper layer, which was rich in cetyl alcohol, was dissolved in petroleum ether after washing it with water and distilling off the amyl alcohol. Since we supposed that the separated lower layer would still be rich in cetyl alcohol, we likewise treated this layer with petroleum ether. The extract obtained was combined with that which was obtained from the upper layer and was washed with warm water. The petroleum ether was distilled off from this and the residue was distilled over in the vacuum still.

Upon cooling the distillate, the cetyl alcohol was obtained as a solid, somewhat yellow colored mass with a melting point of 47.8-48.5 C (yield, 65 per cent).

The 1-octadecanol was prepared from the stearic acid ester in a corresponding manner. From 120 g of the ethyl ester of stearic acid, 80 g of 1-octadecanol was obtained. Yield, 77 per cent. Also, this product was not so yellow in color.

#### CONVERSION OF THE ETHYL ESTERS OF PALMITIC- AND STEARIC ACIDS BY THE METHOD OF ADKINS

The ester of palmitic acid, from which we started, was prepared in the same manner as was specified above. After the preparation, this ester, which has a lower melting point, separated as a liquid upper layer, which finally formed a hard cake which was difficult to wash. The first experiment which we carried out with the Adkins catalyst was a failure. Since we thought that the "ester cake" probably contained entrained sulfuric acid, which caused this less favorable result, we first recrystallized the ester of palmitic acid from alcohol. One-hundred grams of this preparation was mixed with 10 g of an Adkins 1) copper chromite catalyst which had been stabilized with barium and heated with hydrogen to 250 C in an autoclave. At room temperature the hydrogen pressure amounted to 100 atm. After an hour, the temperature had increased to 250 C and the pressure was 170 atm. If no hydrogen was used, the pressure at 250 C would be much higher. Therefore, it was apparent from this that the reaction proceeded smoothly. Afterward, hydrogen was introduced at 250 C until a pressure of 260 atm. was reached. This pressure did not diminish while the temperature was kept constant. Accordingly, the reaction was already completed during the heating period of one hour.

The reaction product was worked up by boiling it with alcohol and then filtering it in order to remove the catalyst. As much solid sodium hydroxide was added to the filtrate as would be required to convert all of the ester of palmitic acid, in case this remained completely unconverted, into sodium palmitate. It was heated for an additional half hour on the steam bath. At the end of this time, an equal volume of water was added and

III-53  
2867

1) Adkins, H. and Connor, R., J. Am. Chem. Soc., 53, 1091 (1931).

the entire mixture was shaken with petroleum ether. After this, the petroleum ether was shaken with warm water for the removal of dissolved soap. After distilling off the petroleum ether, the cetyl alcohol was distilled over in a vacuum still. The product which distilled over solidified into a colorless mass. Melting point, 48.5-49.2 C. Accordingly, it is purer than the product obtained with the procedure of Bouveault and Blanc. The yield amounted to 77 g (90 per cent).

The results of the conversion of the ester of stearic acid are not yet known and will be disclosed in the next report.

### CONCLUSIONS

We have converted palmitic acid and stearic acid into cetyl alcohol and 1-octadecanol, respectively, by means of their ethyl esters. We have carried out the preparation of these substances by two different procedures, namely

1. according to the method of Bouveault and Blanc, which we have changed somewhat according to the example of Bleyberg and Ulrich, and
2. according to the method of Adkins.

The latter method gives somewhat the better results, and, in addition, it can be carried out much more simply than is the case with the procedure of Bouveault and Blanc.

### PLANNED ADDITIONAL RESEARCH

We will convert 1-octadecanol into hexatriacontane ( $C_{36}H_{74}$ ) via the bromide.

February, 1943

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### PREPARATION OF STEARIC ACID

- a. Working Up the Solid Part of the Ester Obtained from the Mixture of Palmitic and Stearic Acids Which Is Rich in Oleic Acid.

In the report for October - November, 1942, the separation of pure palmitic acid and pure stearic acid from a mixture of the methyl esters of palmitic acid, stearic acid, and oleic acid was described. It was reported that the mixture of methyl esters, which was obtained by esterification of a technical mixture of palmitic acid and stearic acid, which is rich in oleic acid with methyl alcohol, can be separated into a solid and a liquid part, and that a sample of the solid part was vacuum distilled. From the fractions of the esters of palmitic acid and stearic acid obtained in this way, we were able to prepare pure palmitic acid and pure stearic acid.

Since the distillation of the entire supply of solid ester has now

been completed, a short summary of the results will be given in this report.

The distillation was carried out in a Vigreux column which was 3 meters long. Pressure, 10 mm Hg. At the beginning, on the plateau, it was distilled at a rate of 100 ml per hour and near the cut point, at 35 ml per hour. The large intermediate fraction between the palmitic acid ester fraction and the stearic acid ester fraction was already mentioned in the report for October - November, 1942. That is, 1600 ml of palmitic acid ester fraction, 500 ml of intermediate fraction, and 800 ml of stearic acid ester fraction were obtained. The question as to the composition of this large intermediate fraction now had to be considered. It was assumed that it consisted of unesterified palmitic acid, as well as oleic acid and oleic acid ester. Therefore, the acid number and iodine number of this fraction were determined. The acid number of palmitic acid is 219. Thus the product contains approximately 5 per cent of unesterified acid. The iodine number was 7.0. The iodine number of oleic acid is 90.1. Therefore, there is neither much oleic acid nor oleic acid ester present. Accordingly, the large intermediate fraction was probably caused by too rapid a distillation. Therefore, the intermediate fraction was redistilled; however, it was now distilled much more slowly, namely, 60 ml per hour on the plateau, from which it developed that 53 per cent of the intermediate fraction consisted of the palmitic acid ester and 28 per cent of the stearic acid ester, while a new intermediate fraction of 12 per cent (calculated on the basis of the total yield) resulted.

The slow distillation of the intermediate fraction has thus shown that the preceding distillation was carried out much too rapidly. On this basis, in the following distillation, it was distilled at 60 ml per hour on the plateau and at 20 ml per hour near the cut point.

On the stearic acid ester plateau, the distillation could be carried on much more rapidly. In distilling the remainder, always take off a small preliminary fraction before taking off the palmitic acid ester, a small final fraction after distilling off the stearic acid ester. The residue was very slight. The boiling point of the methyl ester of palmitic acid is 171 C at 10 mm Hg. The boiling point of the methyl ester of stearic acid is 192 C at 10 mm Hg.

b. Working Up the Liquid Part of the Ester Obtained from the Mixture of Palmitic Acid and Stearic Acid Which Is Rich in Oleic Acid.

In the report for October - November, 1942 it was assumed that the liquid part of the ester, obtained by the esterification of the mixture of palmitic acid and stearic acid which is rich in oleic acid, consists to a considerable extent of oleic acid ester. With subsequent investigation it turned out that this product had an appreciable iodine number, namely 18.1 (the iodine number for oleic acid is 90.1).

The liquid mass of ester was now hydrogenated by heating 9107 g of the ester together with hydrogen in a rotating autoclave to 100-110 C, using 5 per cent nickel on kieselguhr as the catalyst. This temperature was reached within half an hour, in which time it was found that practically all the hydrogen required was taken up. The maximum working pressure amounted to 245 atmospheres.

After cooling, the molten reaction product was filtered on a steam heated Büchner funnel for separation of the catalyst. The filtrate was a nearly colorless liquid, which upon cooling changed into a slightly green colored solid material. Perhaps the green color resulted from a small amount of nickel soap which formed.

As was mentioned in our report for October - November, 1942, we then distilled the mixture of fatty acids obtained by hydrogenation of a mixture of palmitic acid and stearic acid which was rich in oleic acid. From this it became evident that decomposition of the hydrogenation product set in during the distillation, and that this was not the case with an unhydrogenated acid mixture. At that time we attributed this to the presence of traces of nickel in the hydrogenated acids.

As we now observed that the product obtained by hydrogenation of the liquid methyl ester was slightly green colored, we did not risk fractionating this product; we first distilled it rapidly under vacuum in order to free the hydrogenation product of the traces of nickel in this way. As a result, we obtained a colorless distillate which, upon cooling, solidified to a solid mass, which was no longer green colored. This distillate was now redistilled.

Results of the Redistillation of the Hydrogenated Ester

Charge	:	7740 g	
First light oil	:	360 ml	
Palmitic acid ester fraction	:	4470 ml	Freezing point, 26.5-28.0 C.
Intermediate fraction	:	300 ml	
Stearic acid ester fraction	:	3250 ml	Freezing point, 35-38 C
Kettle residue	:	50 ml	

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We carried out the redistillation again in a column which was 3 meters long; pressure, 10 mm Hg. During the redistillation no decomposition occurred. Take-off rate: 60 ml per hour on the plateau and 20 ml per hour in the vicinity of the cut point.

From the results of the redistillation, the following may be concluded:

The methyl esters which had been hydrogenated are richer in

stearic acid and poorer in palmitic acid than the so-called solid methyl esters.

The intermediate fraction is much smaller than with the so-called solid methyl esters.

The freezing point of the palmitic acid ester fraction is lower than that of the palmitic acid ester obtained from the so-called solid methyl esters.

The freezing point of the stearic acid ester fraction is higher than that of the stearic acid ester obtained from the so-called solid methyl esters.

However, it can be concluded from the entire results of the redistillation of the methyl esters of a mixture of palmitic acid and stearic acid, which was rich in oleic acid, that it is not necessary to divide the methyl esters into a solid and a liquid part; it is much simpler if one hydrogenates the entire mixture of esters; after that, vacuum distills and finally redistills.

#### PREPARATION OF 1-OCTADECANOL FROM THE ETHYL ESTER ACCORDING TO THE METHOD OF ADKINS

In the report for December, 1942, the preparation of cetyl alcohol from the ethyl ester of palmitic acid was described, among other things. This method was now also applied in the same manner with the ethyl ester of stearic acid, with which we have carried out two experiments. One was carried out with 10 per cent of the Adkins catalyst, exactly the same as we used with the ester of palmitic acid. In another experiment, we used 5 per cent of the Adkins catalyst.

In the first case, in which we started with 100 g of stearic acid ester, 68 g of 1-octadecanol; and in the second case, 70 g (theoretical, 86.5 g), were produced. Since it turned out that the conversion of the esters of palmitic- and stearic acids into the  $C_{16}$  and  $C_{18}$  alcohols were nearly quantitative, a much simpler method was observed in working up the  $C_{18}$  alcohol than in the preparation of cetyl alcohol. Namely, the reaction product was boiled with methylethylketone and subsequently filtered. The catalyst remained behind on the filter, while the  $C_{18}$  alcohol crystallized out of the filtrate in magnificent, lustrous, white, small, leaf-like crystals. Still more of the 1-octadecanol could be obtained from the mother liquor of this alcohol by distilling off a portion of the methylethylketone.

March, 1943

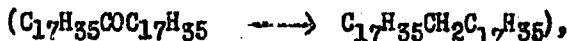
#### CONVERSION OF STEARONE INTO N-PENTATRIACONTANE

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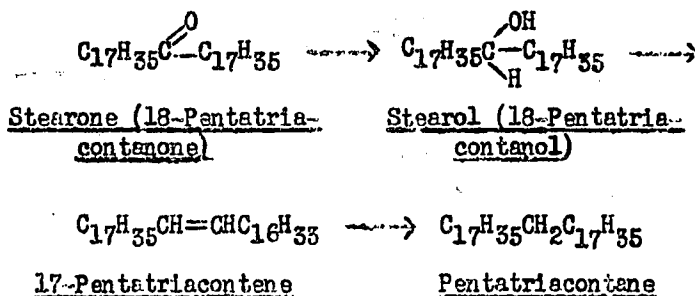
#### INTRODUCTION

In the report for December, 1942 (page III-46), the preparation

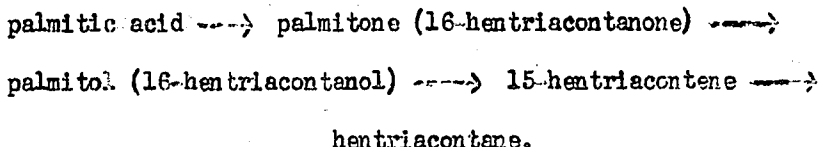
of stearone was described. The next step was the conversion of this ketone into n-pentatriacontane,



for which we chose the method of Clemmensen (reduction with nascent hydrogen, obtained from amalgamated Zn : HCl). However, this method gave a very unsatisfactory result, so we looked around for another procedure. The following procedure appeared to us to be more successful:



However, since our supply of stearic acid was limited, we first chose to use this reaction once with palmitic acid according to the scheme:



#### SUMMARY OF THE INVESTIGATION

The result of the Clemmensen reduction was very unsatisfactory, i.e., the yield of hydrocarbon was very small.

The experiment was carried out in the following manner: amalgamated zinc and hydrochloric acid were added to the ketone to be reduced. The entire charge was heated while being vigorously stirred. The ketone melted and floated as an upper layer upon the hydrochloric acid. The stirring was supposed to bring about contact between the ketone and the nascent hydrogen on the zinc. Since it was not performed in a homogeneous medium, only a small amount of the hydrogen generated was utilized for the desired object. One would now be inclined to add any solvent, e.g., alcohol or acetic acid, by means of which the solubility of the upper layer in the lower layer would be increased, and by means of which a more rapid conversion of the ketone into the alcohol could be effected. However, we do not find any optimistic reports about this in the literature; namely, it is mentioned therein that with the addi-

tion of the solvent in question, a strong resinification appears during the reduction. Because of this, we discontinued this experiment also.

The conversion of stearone into n-pentatriacontane was carried out with the help of amalgamated zinc and hydrochloric acid by Backer and Strating \*). However, these investigators obtained no yield.

However, it is known that the method of Clemmensen gives a better result for aromatic ketones than for aliphatic ketones. As a preliminary test for the reduction of stearone to the hydrocarbon via the secondary alcohol (stearol), we prepared a quantity of palmitone from palmitic acid, and determined that the reduction to palmitol with hydrogen at 120 atm. proceeds very well at 100 C in the presence of nickel on kieselguhr.

### CONCLUSIONS

The Clemmensen procedure for the reduction of stearone to  $C_{35}H_{72}$  is not suitable for our purpose. Therefore, we looked around for another method and chose the indirect reduction (conversion of the ketone into the secondary alcohol, dehydration, and hydrogenation).

Of these reaction steps, the reduction to the secondary alcohol proceeds smoothly, as can be demonstrated in the case of the conversion, palmitone  $\longrightarrow$  palmitol.

### PLANNED ADDITIONAL RESEARCH

Starting out with the palmitol obtained, we will try to determine if the reactions chosen for the production of the hydrocarbons are really practical, and then use these reactions with stearone.

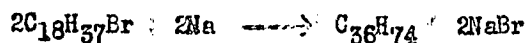
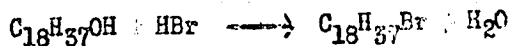
April, 1943

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### A. PREPARATION OF n-HEXATRIACONTANE

#### INTRODUCTION

Since we now have a quantity of 1-octadecanol at our disposal (refer to the February report, page III-63), we have subsequently undertaken the preparation of n-hexatriacontane. We intended to carry out the conversion of 1-octadecanol according to the method of Ruhoff, Burnett, and Reid \*\*):



\*) Rec. trav. chim., 59, 935 (1940).

\*\*\*) J. Am. Chem. Soc., 56, 2784 (1934).

Since some difficulties arose in the preliminary experiments, we first used the procedure with another less expensive alcohol, namely commercial cetyl alcohol (1-hexadecanol).

#### SUMMARY OF THE INVESTIGATION

In the method of Ruhoff, which was cited above, gaseous HBr is passed into the alcohol, which is heated to 100-120 C. After that the bromide formed was purified by treatment with strong sulfuric acid. In order to reduce the appearance of emulsions -- caused by the presence of sulfuric acid esters -- in the neutralization, a solution of ammonia in diluted methyl alcohol was added instead of an alkali solution. Moreover, the use of methyl alcohol has the advantage that a better separation of the layers is obtained, because the difference in density between the bromide and the methyl alcohol is greater than that between the bromide and water.

However, our experience with the procedure of Ruhoff, which was cited above, is less favorable. Namely, in the preparation of the bromide, water is formed, which is separated with difficulty. Owing to this, the already dark colored product becomes still darker because of the development of heat on addition of the sulfuric acid required for the necessary refining. A separation of the sulfuric acid layer and the bromide layer is very difficult because of this.

We obtained better results with this when we carried out the reaction of the alcohol with HBr at 150 C. At this higher temperature, the water formed evaporated. After completion of the reaction, we first vacuum distilled the dark colored product, and after that, treated the colorless distillate with sulfuric acid. After drawing off the sulfuric acid, it was neutralized with ammonia dissolved in methyl alcohol. However, with this, a pronounced emulsification resulted, so that the bromide layer could be separated from the methyl alcohol layer only after standing for several days. III-90  
2911

In consideration of the experience gained in the cetyl bromide preparation, the conversion of 1-octadecanol was likewise carried out at 150 C. Afterward, the product obtained was vacuum distilled without further purification. We omitted the sulfuric acid refining at this point because the bromide yield amounted to 90 per cent, so that less unconverted product was present. In addition, since the bromide is solid at room temperature, this treatment must be carried out at higher temperature, and, for this reason, the product would be acted on by the sulfuric acid.

The procedure employed in the experiment was as follows:  
88 g of 1-octadecanol was heated to 150 C in a flask and then HBr was introduced. After 70 minutes, the increase in weight amounted to 16 1/2 g; after 90 minutes, 17 1/2 g; and after 110 minutes, 17 g. Accordingly, the weight diminished, which may be traced back to a partial evaporation of the



1-bromooctadecane. Therefore, after 110 minutes, the introduction of HBr was stopped, and the reaction product was distilled in a vacuum still. The 1-bromooctadecane distilled over between 186 and 193 C at 4 mm Hg. It is a colorless liquid, which soon becomes solid. A little very dark colored residue remained in the distillation flask. The yield amounted to 96 g (90 per cent).

### CONCLUSIONS

1-Bromooctadecane can be prepared with a very good yield by saturating 1-octadecanol with HBr at 150 C and then distilling.

### B. CONVERSION OF STEARONE INTO n-PENTATRIACONTANE

#### INTRODUCTION

As was mentioned in the preceding report (page III-76), we wished to examine the possibility of converting stearone (18-pentatriacontanone) via stearyl (18-pentatriacontanol) into n-pentatriacontane, first with the help of palmitone (16-hentriacontanone). An attempt was now made to convert the palmitol (16-hentriacontanol), which we had prepared from palmitone (16-hentriacontanone), into n-hentriacontane, with which we followed the procedure in which secondary alcohols in general are dehydrated by heating with  $\text{KHSO}_4$  at 170-180 C.

#### SUMMARY OF THE INVESTIGATION

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2915

A flask, to which a mixture of 110 g of palmitol (16-hentriacontanol) and 20 g of  $\text{KHSO}_4$  had been added, was heated on an oil bath at 170-180 C for 3 hours. Because absolutely none of the water formed could be seen, we added 10 g more  $\text{KHSO}_4$  and heated for another 1 1/2 hours. After cooling, it became evident that the palmitol (16-hentriacontanol) somewhat contaminated with  $\text{KHSO}_4$ , which does not count - remained unchanged. A repetition of the experiment, which, however, was now carried out by heating at 250 C under vacuum, gave a partial decomposition of the palmitol (16-hentriacontanol), whereas the rest remained unconverted.

May, 1946

III-97  
2922

### PREPARATION OF HEKATRIACONTANE (Continuation from page III-90)

#### INTRODUCTION

Several years ago, a method for the conversion of alkyl halides into hydrocarbons with double the number of carbon atoms was published by Oldham and Ubbelohde <sup>1)</sup>, in which the alkyl halides in ether solution

1) J. Chem. Soc., 201 (1938).

were first treated with magnesium and after that with iodine. A part of the halides is thereby converted into the corresponding hydrocarbon by the Wurtz reaction; another part is converted into a Grignard compound, which with the addition of iodine, forms the iodide, which again with magnesium brings about the Wurtz reaction. By this procedure, suitable yields (65 per cent) were obtained. However, since we did not have a sufficient quantity of iodine at our disposal, we used the older method, in which the alkyl halides are converted into hydrocarbons with double the number of carbon atoms with the use of sodium.

#### SUMMARY OF THE INVESTIGATION

To a flask was added 174 g of 1-bromooctadecane and 18.5 g of sodium (theory, 15.2 g). On heating in the oil bath, the reaction began at a temperature of 100 C, which was indicated by the rise of the internal temperature to 170 C (outside temperature, 110 C). After some time, the internal temperature fell; after that, it was heated for another 8 hours at 150 C. Then the excess sodium was made harmless by refluxing for several hours with 60 ml of alcohol. The sodium reacted extremely slowly with the alcohol under these conditions. Finally, 150 ml of water was added to dissolve the NaBr which had formed.

The upper layer, which had become solid on cooling, was withdrawn and afterward melted with alcohol. After the hydrocarbon had again become solid, it was withdrawn again and recrystallized from methylethylketone to a yellow mass with a melting point range of 70-73 C, with a yield of 53 per cent.

Since the pure hydrocarbon has a melting point of 75.8 C (refer to Report 6568 by Dr. Mazee), we repurified this product by heating it for an hour at 130 C with a six-fold amount by weight of strong sulfuric acid, and afterward recrystallizing it from benzene. The product obtained, which consisted of rather dark colored small leaf-like crystals, could be decolorized with Terrana\* in benzene solution. The yield of this pure hydrocarbon, which had a melting point of 75.6-75.9 C, amounted to 35 per cent.

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#### CONCLUSIONS

n-Hexatriacontane can be obtained with a 35 per cent yield by conversion of 1-bromooctadecane with sodium.

June, 1943

III-123  
2951

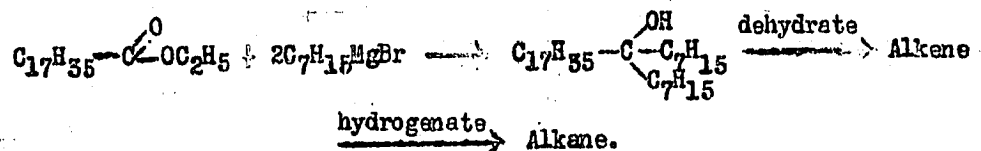
#### PREPARATION OF A BRANCHED ALIPHATIC HYDROCARBON WITH A LONG SIDE CHAIN

#### INTRODUCTION

In the monthly report for May, 1942 (page III-12), it was re-

\* Translator's note: Probably some special adsorbent clay.

ported that it was the intention to prepare 8-n-heptylnonacosane as an example of a branched aliphatic hydrocarbon with a long side chain. According to the reaction scheme described therein, we planned to start out with erucic acid. Since this acid is not available under present circumstances, we used stearic acid as the only other available raw material with a large number of carbon atoms. With this starting material, we could prepare 8-n-heptylpentacosane according to the following scheme:



Since our supply of stearic acid is limited, we have - because this reaction was not found in the literature - next carried out a short experiment with the ester of palmitic acid. Since it turned out in this case that the ester remained largely unchanged in the reaction mixture, we decided to try the reaction first with phenylmagnesiumchloride, since our supply of 1-bromoheptane is rather limited. In addition, the reaction product of the palmitic acid ester with phenylmagnesiumbromide is a solid material, so that it may easily be isolated in pure form.

The reaction of the palmitic acid ester with phenylmagnesiumbromide has been described repeatedly in the literature:

Ryan and Dillon 1) prepared the 1,1-diphenyl-1-hexadecanol.  
Wienhaus and Treibe 2) likewise carried out the reaction; however, they mentioned few details.  
Skraup and Schwamberger 3) mention that the palmitic acid ester reacts very slowly, so that the reaction must be continued for a long time.  
Fierz and David 4) likewise allow the ester to react for a long time with phenylmagnesiumbromide.  
Schmidt and Hartmann 5) used an excess of phenylmagnesiumbromide.  
Wibaut, Overhoff, and Jonker 6) prepared 1,1-diphenyl-1-hexadecanol; however, they obtained a very impure product.

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#### SUMMARY OF THE INVESTIGATION

##### 1. PREPARATION OF 1,1-DIPHENYL-1-HEXADECANOL

We used bromobenzene which had been dried with calcium chloride and subsequently distilled, and the ethyl ester of palmitic acid which had been recrystallized once from alcohol and finally dried under vacuum over  $\text{P}_2\text{O}_5$  as starting materials.

- 1) Proc. Roy. Irish Acad., B 29, 235 (1911-1912). - This literature is not available at present.
- 2) Ber., 56, 1648 (1923).
- 3) Ann., 462, 136 (1928).
- 4) Helv. Chim. Acta., 22, 82 (1939).
- 5) Ber., 74, 1325 (1941).
- 6) Rec. trav. chim., 62, 31 (1943).

To a round-bottom flask was added 13.4 g of magnesium, 6 ml of ether which had been dried over sodium wire, as well as a crystal of iodine. A mixture of 81.6 g of bromobenzene (0.51 mole) and 200 ml of dry ether was allowed to trickle from the dropping funnel into the reactor in 1 1/2 hours. Afterward, it was stirred for another half hour while the flask was heated until the ether refluxed gently. Then a solution of 68 g of the palmitic acid ester (0.24 mole) in 150 ml of dry ether was added at room temperature during a period of 1/2 hour. It was stirred for 1/2 hour with heating. Afterward, the flask was placed in ice and 150 ml of ice water, and later, 120 ml of 1:1 hydrochloric acid were added. The ether layer was then separated from the aqueous layer and the aqueous layer was extracted several times with ether. The combined ether extracts were washed with water. It is not advisable to shake the ether layer with soda solution because an emulsion is formed in this way. After distilling off the ether, the residue was dissolved in 200 ml of alcohol. Nothing would crystallize out of this solution. On cooling with ice and salt, quite a lot crystallized out. This product melted in the range, 42.0-44.9 C, and was accordingly very impure. The impurity probably consisted of the unconverted palmitic acid ester. For removal of this impurity, the product was dissolved in the mother liquor, an equal volume of water and 1 1/2 g of KOH were added, and the mixture was boiled on the steam bath. After cooling, the product which had crystallized out was filtered off, washed with 60 per cent alcohol (for washing out the potassium palmitate), and afterwards recrystallized from alcohol. The product obtained in this way melted at 45-48 C and, therefore, was somewhat purer.

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In an additional experiment, we started with palmitic acid ester, which was vacuum distilled after one recrystallization from alcohol. After the addition of the palmitic acid ester to the phenylmagnesiumbromide, it was stirred for 3 more hours while being heated.

After distilling off the ether, the residue was heated for one hour with a solution of 1 1/2 g of KOH in 200 ml of 50 per cent alcohol. After the contents of the flask had cooled, they were drawn off and twice recrystallized from alcohol. Forty-six and one-half grams of 1,1-diphenyl-1-hexadecanol (theory, 94 g) was obtained, with a melting point of 48.5-49.4 C; accordingly, this was much purer than the product obtained in the first experiment. Somewhat more of the product can still be obtained from the mother liquor. The 1,1-diphenyl-1-hexadecanol, after repeated recrystallization from alcohol, melted at 48.7-49.4 C.

Melting points between 43 and 49 C are mentioned in the literature.

From our experiments, it is evident that it is advisable to allow the ester to react with the phenylmagnesiumbromide for a longer period of time.

## 2. PREPARATION OF 1-BROMOHEPTANE

Analogous to the preparation of 1-bromooctane described by Asmus 1), we have converted 1-heptanol into 1-bromoheptane with 48 per cent

1) Organische Synthesen, 24 (1937).

HBr in the presence of sulfuric acid. The 48 per cent HBr solution is obtained by passing a rapid stream of  $\text{SO}_2$  into a mixture of 250 g of water, 750 g of ice, and 600 g of bromine in such a way that the incoming gas is introduced under the surface of the bromine; as soon as the liquid has become yellow colored, the introduction of  $\text{SO}_2$  is stopped and then the solution is distilled. Of the distillate, the colorless part which distilled over between 125 and 126 C was refluxed with 1-heptanol for 6 hours. After working it up and vacuum distilling, a product with  $n_D^{20} = 1.4501$  and a boiling point of 80 C at 28 mm Hg was obtained, with a yield of 80 per cent.

The preparation can also be carried out very well with gaseous HBr according to the method of Ruhoff 1) instead of with the HBr solution.

### 3. PREPARATION OF n-HEPTYLMAGNESIUMBROMIDE

In carrying out the reaction of the palmitic acid ester with heptylmagnesiumbromide, we noticed that it was less successful. By means of the investigation described under 2), the reason was cleared up, at least partially. We observed from this that the ester must react with the Grignard compound for a longer period of time. The question regarding the preparation of n-heptylmagnesiumbromide from 1-bromoheptane now arose.

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It was indicated in the literature (among others, Johnson and Adkins 3); Gilman, Zoellner, and Dickey 4); and Gilman and McCracken 5) that 1-bromoheptane will form the Grignard reagent very readily.

In our experiments, a solution of 20 g of 1-bromoheptane in 25 ml of ether was added dropwise to 50 ml of ether which had been dried over sodium wire. After this entire preparation had stood for a week in a nitrogen atmosphere, it was determined by titration that 55 per cent had been converted into the Grignard compound. Although we know that this conversion is greatly influenced by the nature of the magnesium used, we have carried out no additional experiments, because, for the present, no other grades of magnesium are available.

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### PREPARATION OF PENTATRIACONTANE

#### INTRODUCTION

In the report for April (page III-90-91), it was reported that we were unsuccessful in dehydrating palmitol (16-hentriacontanol) with  $\text{KHSO}_4$ .

- 1) J. Am. Chem. Soc., 56, 2784 (1934).
- 2) Organische Synthesen, 24 (1937).
- 3) J. Am. Chem. Soc., 54, 1943 (1932).
- 4) J. Am. Chem. Soc., 51, 1576 (1929).
- 5) J. Am. Chem. Soc., 45, 2464 (1923).

We then carried out another experiment with a great excess of potassium hydrogen sulfate (10 g of palmitol and 20 g of  $\text{KHSO}_4$ ). In this case, just as little water was formed and on working up the product, the palmitol was recovered unchanged.

We now decided to try to convert the palmitol into 15-hentriacontene by pyrolysis of the 16-hentriacontanol acetate (palmitol acetate).

#### SUMMARY OF THE INVESTIGATION

##### A. PREPARATION OF 16-HENTRIACONTANOL ACETATE

Ten grams of palmitol was refluxed for an hour with 50 g of acetic anhydride, to which 5 g of anhydrous sodium acetate had been added. After cooling, it was poured out into water and the solid material was removed. By recrystallization from alcohol, a colorless powder with a melting point of 53.6-54.3 C was obtained; the yield was 9.8 g (90 per cent).

##### B. PREPARATION OF 15-HENTRIACONTENE

We carried out the pyrolysis as a vacuum distillation in order that the 15-hentriacontene formed would be exposed for as short a time as possible to the high temperature, and the tendency to isomerize would be reduced to a minimum in this way.

The first experiment was carried out in a Claisen flask with a conical bottom; it was distilled therein under the vacuum produced by a water pump. From a flask, which was heated to 250 C, nothing distilled over at a pressure of 23 mm Hg. By heating with the open flame, most of the contents of the flask distilled over. Since the pressure gradually increased during the experiment, the distillation proceeded more and more slowly. After recrystallization of the distillate from alcohol, a colorless solid material melting between 47 and 55 C was obtained.

A second experiment was carried out in the vacuum still, but in addition, we passed the pyrolysis product distilling over through a layer of glass wool heated to 450 C in order to cleave still more of the undecomposed acetate remaining. The distillation flask was heated over the open flame, while the receiver was immersed in ice. During the distillation, the pressure increased from 3 mm to 25 mm Hg. Because the distillation at this pressure proceeded too slowly, we stopped the distillation for a short time in order to lower the pressure before continuing the experiment. A total of 30 g of 16-hentriacontanol acetate was subjected to pyrolysis; in this way, an 80 per cent yield of 15-hentriacontene was obtained. However, it should be noted that the product obtained is not a single compound, but that it is a mixture of cis- and trans isomers. There is no reason for separating the pyrolysis products

because on hydrogenation, both isomers are converted into hentriacontane.

### C. PREPARATION OF HENTRIACONTANE

Thirty-three grams of 15-hentriacontene was dissolved in 300 ml of cyclohexane; afterward, platinum oxide, according to Adams, was added and the mixture was shaken with hydrogen until no more of it was taken up.

At the expiration of the hydrogenation reaction, a portion of the hydrogenation product had already crystallized out. A significant amount of the reaction product could still be obtained from the mother liquor. For purification, the entire product was heated for an hour at 130 C with a six-fold quantity of sulfuric acid. After cooling, the material which separated out was drawn off, washed with water, and recrystallized from benzene. The product which was obtained in this way, which was still somewhat yellow colored, could be completely decolorized in benzene solution with Terrana. After recrystallization from benzene to a constant melting point, a product with a melting point of 67.5-67.8 C was obtained. (Kraft<sup>1</sup>) mentioned 68.1 C).

### CONCLUSIONS

Palmitol (16-hentriacontanol) can be converted into 16-hentriacontanol acetate with a good yield by reaction with acetic anhydride in the presence of anhydrous sodium acetate.

15-Hentriacontene can be prepared by distilling 16-hentriacontanol acetate under vacuum.

15-Hentriacontene can be hydrogenated to hentriacontane with the assistance of the Adams catalyst.

<sup>1</sup>) Ber., 40, 4779 (1907).