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High-molecular-weight aliphatic compounds of nitrogen and sulfur

Byron Alexander Hunter
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HIGH-MOLECULAR-WEIGHT ALIPHATIC COMPOUNDS
OF NITROGEN AND SULFUR

by

Byron A. Hunter

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Organic Chemistry

Approved:

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INTRODUCTION

The last decade has seen unusual advances in the realm of aliphatic chemistry. Considerable progress has been made in the field of long-chained compounds, and many substances that were formerly very difficult to obtain in the pure state are now being produced on a commercial basis. With the recent availability of pure long-chained fatty acids and derivatives of these, such as amines, nitriles, ketones, etc., a great impetus has been given to the investigation of the chemical possibilities of these materials. The fatty acids themselves provide the basic materials from which the long-chained aliphatic compounds may be synthesized. Esterification and reduction gives the alcohols. These may be converted to the alkyl halides, which find wide application in the synthesis of long-chained compounds. The acid chlorides are easily produced, and they react smoothly with aromatic compounds to give long-chained aromatic ketones that are gaining increasing importance. The ammonolysis and dehydration of the fatty acids yield the amides and nitriles. The aliphatic nitriles are readily reduced to amines, which form the basis for the synthesis of a variety of long-chained nitrogen compounds.

As a result of the newer researches on fatty acid derivatives, many new substances have been produced which have already found commercial application of considerable importance. The high-molecular-weight amines, for example, are being used as emulsifiers, detergents, and acid-corrosion inhibitors, etc. Long-chained aliphatic-aryl ketones are valuable as waxes and as addition agents for the improvement of lubricants. Several types of long-chained compounds have been suggested as insecticides, insect

repellants, and weed poisons. The fat-solubility of N¹-n-dodecoylsulfenilamide has suggested the possible use of this drug in the treatment of tuberculosis. It has been shown that many long-chained compounds exhibit marked physiological activity. Other compounds derived from fatty acids have interesting properties for which specific uses have not as yet been developed. There is little doubt that many of these will find important application in the future.

This thesis is concerned with the further development of long-chained compounds, particularly of those containing the additional elements of nitrogen and sulfur. The study was undertaken with four general objectives in view: first, to continue the studies initiated in these laboratories several years ago concerned with establishing the limits of homology as applied to the reactions and physical properties of high-molecular-weight fatty acid derivatives; second, to investigate the possibilities of certain new compounds as derivatives for the identification of long-chained molecules; third, to develop techniques for applying the reactions of short-chained aliphatic compounds to long-chained homologs; and fourth, to produce new compounds which either would be commercially useful themselves or would serve as intermediates for further work in that direction.

HISTORICAL

Nitrogen Compounds

I. Carboxylic Acid Salts and Amides of n-Dodecylamine and n-Octadecylamine.

The distinctly basic character of aliphatic amines is demonstrated by the ease with which they form salts of both inorganic and organic acids. Methylamine, for example, reacts quickly with carboxylic acids such as acetic, phenylacetic, palmitic, succinic, tartaric, benzoic, phthalic, and hippuric to form the corresponding salts (1). The salts are crystalline substances which usually undergo dehydration to the amides upon heating. Ralston and co-workers (2,3) have prepared a number of carboxylic acid salts of higher-molecular-weight amines. Some of these exhibit properties that make them useful as wetting agents, detergents, bactericides, or insecticides. A concentration of ten parts per million of dodecylamine acetate produces flocculation of suspended particles in turbid water so that a clear solution is obtained after filtration (2).

Most of the carboxylic acid salts of aliphatic amines undergo pyrolytic dehydration to amides. This reaction has been known since the early work of Wurtz (4) who distilled dimethylammonium oxalate to form dimethyl oxamide. Using a similar procedure, Linnemann prepared methyl,

- (1) Gibbs, J. Am. Chem. Soc., 28, 1409 (1906).
- (2) Ralston, Oil and Soap, 17, 89 (1940).
- (3) Ralston, Barrett and Hopkins, ibid., 18, 11 (1941).
- (4) Wurtz, Ann. chim., 30, 464 (1850).

ethyl and diethyl formamide from the corresponding formic acid salts (5).

Decomposition of acetic acid salts of a number of lower primary and secondary amines was quantitatively studied by Musselius (6). The salts were heated in sealed tubes at 215° for thirty minutes and the unchanged salt was determined by titration with base. He found that the yield of the amide increased with the molecular weight of the amine.

The isolation of the amine salts is not essential, as was shown by Franchimont and Klobbie (7) who heated a number of low-molecular-weight amines with heptylic acid in sealed tubes to obtain the desired amides. Mitchell and Reid (8) prepared the dimethyl amides of the normal fatty acids from formic to heptic by passing dimethylamine through the acids at temperatures ranging from 95° to 160° for varying lengths of time, the conditions depending on the acid used. Various modifications of this general procedure have been used to prepare N-alkyl substituted amides. Several propionamides were prepared by Bowen and Smith (9) by refluxing the amines with propionic acid for several hours. A U. S. Patent (10) refers to the production of substituted amides by heating aliphatic acids with aliphatic amines in the presence of a liquid immiscible with water. A constant boiling mixture is thus produced which may be distilled off,

- (5) Linnemann, Sitzber. Akad. Wiss. Wien, 60, 44 (1870),
[Chem. Zentr., 41, 138 (1870)]
(6) Musselius, J. Russ. Phys. Chem. Soc., 32, 29 (1900),
[Chem. Zentr., 71, [I], 1071 (1900)]
(7) Franchimont and Klobbie, Rec. trav. chim., 6, 241 (1887).
(8) Mitchell and Reid, J. Am. Chem. Soc., 53, 1879 (1931).
(9) Bowen and Smith, ibid., 62, 3522 (1940).
(10) U. S. Patent 1,954,453 [C. A., 28, 3741 (1931)]

removing the water formed in the reaction. Concurrent with the work reported in this thesis, Harber (11) has prepared a number of long-chained N-substituted amides by heating n-dodecyl- and n-octadecylamine directly with carboxylic acids. Among those described were o- and p-chlorobenzamides, o- and m-toluamides, oleamides, elaidamides and anisamides of these amines. N,N'-Di-n-octadecyl malonamide and N-n-dodecyl and N-n-octadecyl phthalimide were also reported by the same investigator.

Aside from the citations given, literature references to the production of long-chained amides from pyrolysis of long-chained amine salts, or by direct formation from the long-chained amines and carboxylic acids, are confined to vague declarations in the patent literature. However, many of the amides have been prepared by less direct methods. N-n-Dodecyl lauramide has been prepared from a mixture of lauramide and lauric acid by heating with hydrogen at elevated temperature and pressure in the presence of a catalyst (12). Adam and Dyer (13) prepared N-n-octadecyl acetamide and N-n-hexadecyl acetamide by warming the corresponding amines with acetic anhydride. N-n-Dodecyl acetamide is described in the patent literature as having been prepared by heating laurionitrile and acetamide with hydrogen under pressure in the presence of nickel (14).

(11) Harber, Doctoral Dissertation, Iowa State College (1940).

(12) German Patent 667,627 [C. A., 33, 2906 (1939)].

(13) Adam and Dyer, J. Chem. Soc., 127, 73 (1925).

(14) British Patent 458,454 [C. A., 31, 3501 (1937)].
German Patent 650,664 [ibid., 32, 953 (1938)].

N-n-Dodecyl benzamide, N-n-dodecyl phenylacetamide and N,N'-di-n-dodecyl oxamide were prepared by Grunfeld (15) from n-dodecylamine and the corresponding ester. N-n-Octadecyl benzamide has been previously prepared by the action of benzoyl chloride on n-octadecylamine (16,18). Hoyt (17) prepared N-n-octadecyl stearamide from stearoyl chloride and n-octadecylamine. Chloroacetic amides of dodecyl-, tetradecyl- and octadecylamine are mentioned in the patent literature (19) but the physical constants and methods of preparation are not given.

A number of amides from long-chained amines other than n-dodecylamine and n-octadecylamine has been reported. Turpin (20) prepared N-n-heptadecyl benzamide from n-heptadecylamine and benzoyl chloride. Jeffreys (21) used the same method to form N-n-pentadecyl benzamide from n-pentadecylamine. The acetyl derivatives of these same amines as well as that of n-undecylamine have been described by Naegeli and co-workers (22). These latter investigators also reported the formation of N-n-heptadecyl stearamide and N-n-pentadecyl palmitamide.

- (15) Grunfeld, Ann. chim., 10, 20, 366 (1933).
- (16) Hoyt, Doctoral Dissertation, Iowa State College (1940), p. 78.
- (17) Ibid., p. 83.
- (18) Shinozaki and Kubo, J. Agr. Chem. Soc. Japan, 13, 1 (1937),
C. A., 31, 3002 (1937).
- (19) French Patent 735,647 [Chem. Zentr., 104, 1224 (1933)].
- (20) Turpin, Ber., 21, 2486 (1888).
- (21) Jeffreys, Am. Chem. J., 22, 23 (1899).
- (22) Naegeli, Gruntuch-Jacobsen and Lendorff, Helv. Chim. Acta,
12, 227 (1929).

Long-chained acids and various amines other than those of high-molecular-weight have been used in the synthesis of a number of amides. de'Conno (23) mixed equimolar amounts of higher fatty acids and aromatic amines and heated these in evacuated, sealed tubes at 230° for five hours. The yields of amides were good. The p-nitro-anilides and 2-nitro-p-toluidides of lauric, myristic, palmitic and stearic acids were prepared by Gilman and Ford (24) by heating the amines with the corresponding acid chlorides. The p-xenylamides of the same acids were prepared by these workers by heating equimolar quantities of the acids and p-xenylamine in sealed tubes for five hours at 135-140°. Robertson (25) prepared the o- and p-toluidides, β -naphthylamides, p-bromoanilides, o-bromo-p-toluidides, α -bromo- β -naphthylamides and 2,4,6-tribromoanilides of a large number of normal fatty acids.

The larger part of the investigation by the author on long-chained amine salts and amides has been published (26). Among the compounds reported were the n-octadecylamine salts of formic, acetic, propionic, butyric, valeric, caproic, caprylic, capric, lauric, myristic, palmitic, stearic, benzoic, anthranilic, α -furoic, cinnamic, salicylic, phenylacetic, oxalic, α -naphthoic and 2-dibenzofurancarboxylic acids. The N-n-octadecyl amides of all the above acids except anthranilic were also included. The n-dodecylamine salts of acetic, propionic, lauric, myristic, palmitic, stearic,

(23) de'Conno, Gazz. chim. ital., 47 [1] 93 (1917),

[C. A., 12, 1172 (1918)].
(24) Gilman and Ford, Iowa State Coll. J. Sci., 13, 135 (1939).

(25) Robertson, J. Chem. Soc., 115, 1210 (1919).

(26) Hunter, Iowa State Coll. J. Sci., 15, 223 (1941).

α-furoic, phenylacetic, α-naphthoic, cinnamic, chloroacetic and 2-dibenzofurancarboxylic acids as well as the corresponding amides of all but the last three were also reported in the same paper.

II. Long-chained N-Alkylpyrrole Derivatives

It is interesting that no pyrrole derivatives containing long-chained alkyl residues have been described in the literature. This might well be ascribed to the fact that pyrrole compounds have been of interest primarily in connection with their relationship to natural substances such as nicotine, atropine, haemoglobin and chlorophyll. Such substances do not contain extended alkyl chains associated directly with the pyrrole nuclei, and hence long-chained pyrroles are not met with in such studies.

The pyrrole derivative with the largest alkyl group that has been reported appears to be 2-n-hexylpyrrole-5-n-caprylic acid (27). This compound was prepared from 9,12-diketostearic acid.

The use of alkyl amines in the synthesis of pyrroles was introduced by Bell (28) who prepared N-alkylpyrroles by pyrolysis of amine salts of mucic acid. This method, even though it appears to be of general application, has been used in preparing only a limited number of N-substituted pyrroles. N-Isosamylpyrrole is the highest homolog of this series that has been reported (29). Another method of wide application for the synthesis of N-substituted pyrroles involves the interaction of an amine and an

(27) German Patent 180,926 [Chem. Zentr., 78 [17], 916 (1907)].

(28) Bell, Ber., 10, 1861 (1877).

(29) Reichstein, Helv. Chim. Acta., 10, 387 (1927).

α,γ -diketone. Diethyl diacetylsuccinate and acetylacetone are the ketones that have been used most generally. Knorr (30) was the first to show that pyrrole derivatives could be formed from the former diketone, while Paal and co-workers (31) used acetylacetone to make 2,5-dimethylpyrrole and H-substituted 2,5-dimethylpyrroles. As was the case with the method of Bell, no long-chained pyrrole derivatives have been synthesized by this method.

A number of lower pyrrole derivatives have been studied for their possible insecticidal activity (32). The interesting insecticidal properties of certain long-chained nitrogen compounds (3) suggests the possible use of long-chained pyrrole derivatives for this purpose. The compounds described in this thesis were prepared with that possibility in view.

III. The Action of Nitrous Acid on n-Dodecylamine

It has long been known that primary aliphatic amines react with nitrous acid to form alcohols. The reaction takes place in the cold with the evolution of nitrogen, and has been used as a test for primary amines. As Whitmore (33) has pointed out, however, the reaction is never a good preparative method for an alcohol. Methylamine, for example, does not react, and ethylamine gives only a 61% yield of ethyl alcohol (34).

(30) Knorr, Ber., 18, 299 (1885); ibid., 18, 1558 (1885).

(31) Paal, ibid., 18, 2251 (1885); Paal and Schneider, ibid., 19, 558 (1886).

(32) Craig and Hixon, J. Am. Chem. Soc., 53, 187 (1931).

(33) Whitmore, "Organic Chemistry", D. Van Nostrand & Co., New York (1937), p. 192.

(34) Whitmore and Thorpe, J. Am. Chem. Soc., 63, 1118 (1941).

n-Propylamine reacts with nitrous acid to give a mixture of n-propyl alcohol (7.4%), iso-propyl alcohol (32%), and propene (28.4%) (34). With n-butylamine, Whitmore (35) found the reaction products to consist of the following mixture: n-butyl alcohol (25%), sec-butyl alcohol (13.2%), n-butyl chloride (5.2%), sec-butyl chloride (2.8%), n-butenes (36.5%), a trace of butyl nitrites and 7.6% of higher boiling material, tentatively identified as dibutylnitrosoamine. It is quite evident that the reaction is not a simple one and involves molecular rearrangements. This has been verified by a number of workers. Siersch (36) in 1867 treated n-propylamine hydrochloride with silver nitrite and obtained nitrogen and normal and iso-propyl alcohols. Linnemann (37) confirmed these results and postulated the intermediate formation of propylene in the reaction. The experiment was repeated by Meyer and Förster (38) who were able to identify propylene as well as dipropylnitrosoamine among the products. These workers separated the alcoholic fraction into 42% primary and 58% secondary propyl alcohols. From n-butylamine, Meyer and co-workers (39) found that the alcoholic fraction consisted of 71% primary and 29% secondary butyl alcohols. Butenes and dibutylnitrosoamine were also detected. Ray and Rakshit (40) heated n-butylamine nitrite at 75° in a

(35) Whitmore and Langlois, J. Am. Chem. Soc., 54, 3441 (1932).

(36) Siersch, Ann., 144, 140 (1867).

(37) Linnemann, ibid., 161, 44 (1872).

(38) Meyer and Förster, Ber., 9, 535 (1876).

(39) Meyer, Barbieri and Förster, ibid., 10, 132 (1877).

(40) Ray and Rakshit, J. Chem. Soc., 101, 141 (1912).

vacuum and reported that isobutyl alcohol was obtained. The experiments of Whitmore (35) yielded no isobutyl alcohol, but only primary and secondary butyl alcohols. Frentzel (41) reported a 40% yield of n-hexyl alcohol from n-hexylamine, following Linnemann's procedure.

An interesting series of experiments carried out by Adamson and Kenner (42) provide data of value for predicting the products that might be expected from the action of nitrous acid on n-dodecylamine. These workers treated the hydrochlorides from n-amyl- to n-decylamine with silver nitrite and decomposed the amine nitrites by slow distillation. Table I summarizes the results of their experiments.

TABLE I
DECOMPOSITION OF AMINE NITRITES

Amines	<u>n</u> -amyl	<u>n</u> -hexyl	<u>n</u> -heptyl	<u>n</u> -octyl	<u>n</u> -nonyl	<u>n</u> -decyl
Alcohols	50.0%	50.5%	48.3%	46.3%	48.5%	50.0%
Olefins	30.1	28.0	25.4	24.4	24.4	27.4
Nitroso-sec. amine	1.9	2.5	5.3	5.5	9.0	15.3
Primary amine	1.7	1.5	0.8	4.5	1.0	1.1
Primary amine HCl	0.7	1.0	0.5	0.8	0.5	1.4
Yield	<u>84.4%</u>	<u>83.5%</u>	<u>80.3%</u>	<u>81.5%</u>	<u>83.4%</u>	<u>95.2%</u>

While the amount of alcohol produced is fairly constant for different

(41) Frentzel, Ber., 16, 743 (1883).

(42) Adamson and Kenner, J. Chem. Soc., 838 (1934).

amines, it was observed by Adamson and Kenner that the proportion of secondary alcohols diminished as the series was ascended, n-nonyl- and n-decylamine yielding no detectable amount. It might be predicted on this basis that the action of nitrous acid on n-dodecylamine would produce only the normal dodecanol in the alcoholic fraction. Such a result would be of considerable interest as a method of converting the readily available normal long-chained amines to normal alcohols.

IV. Nitration of Long-chained Fatty Acids

In considering ways to broaden the chemical possibilities of long-chained aliphatic compounds, the problem of introducing chemically reactive groups into the saturated hydrocarbon chain immediately present itself. The usual methods of halogenation, sulfonation, and nitration that are very useful in aromatic chemistry are much more limited as methods of introducing reactive groups into saturated aliphatic compounds. Halogenation appears to occur most smoothly, and the Hell-Volhard-Zelinsky method of preparing α -halogen aliphatic acids is well known. The halogenation of relatively low-molecular-weight saturated hydrocarbons is now conducted on a commercial basis (43) and the extension of this reaction to high-molecular-weight hydrocarbons has recently been investigated in studies by Padgett and Degering (44) who have chlorinated the saturated kerosene fraction of petroleum. The sulfonation of saturated aliphatic compounds is still of very little importance and the discussion of this reaction is deferred to a later section of this thesis. Until recently the direct nitration of

(43) Ayers, Ind. Eng. Chem., 21, 899 (1929).

(44) Padgett and Degering, ibid., 32, 204, 486 (1940).

aliphatic compounds has also been considered of little synthetic value. This is due to the fact that the action of nitric acid on aliphatic compounds usually yields a mixture of products and is practically always accompanied by extensive oxidation. Hass and co-workers (45) have succeeded in overcoming many of the difficulties usually encountered in such nitrations by conducting the reaction in the vapor phase. This procedure at present seems to be practical only with relatively low-molecular-weight hydrocarbons and has not been applied to high-molecular-weight compounds.

The earliest studies on the reaction of nitric acid on aliphatic compounds appear to have been made on the fatty acids themselves. In 1846 Redtenbacher (46) heated oleic acid with fuming nitric acid and obtained a mixture of shorter-chained fatty acids. No mention was made of nitro compounds being formed. Dessaigne (47) heated valeric acid with nitric acid and obtained a solid product which gave an analysis that corresponded fairly well with that required by nitrovaleric acid. Erlenmeyer (48) heated caproic acid with concentrated nitric acid for ten days and recovered only a mixture of acetic and dibasic acids.

Several investigators have studied the action of nitric acid of various concentrations on stearic acid. Claus and Pfeiffer (49) heated stearic acid for two days with a mixture of concentrated nitric acid and acetic acid. They state that among the various oxidation products they obtained a yellowish buttery mass in 50 per cent yield that analyzed for

(45) Hass, Hodge and Vanderbilt, Ind. Eng. Chem., 28, 339 (1936).

(46) Redtenbacher, Ann., 59, 44 (1846).

(47) Dessaigne, ibid., 79, 374 (1851).

(48) Erlenmeyer, ibid., 180, 210 (1875).

(49) Claus and Pfeiffer, J. prakt. Chem., [2] 43, 161 (1891).

nitrostearic acid. The product could not be crystallised nor was it distillable either in vacuum or by steam. Among the oxidation products were carbon dioxide and adipic, suberic and sebacic acids. A small amount of water-soluble oily material also recovered was thought to be a mixture of nitroacrylic and nitroacrylic acids. Champion and Pellet (50) introduced stearic acid into a large excess of mixed nitric and sulfuric acids and obtained a slightly yellowish powder that analysed for nitrostearic acid. More recently Badolifte and Polychronis (51) in studying the action of nitric acid on saponifiable oils treated a petroleum ether solution of stearic acid with nitric acid (sp. gr. 1.50) at room temperature and recovered the stearic acid unchanged. In a second experiment these workers treated stearic acid with a mixture of fuming nitric and concentrated sulfuric acids. Here again the material recovered appeared to consist mainly of stearic acid, and nitrogen analyses on the substance gave a very low percentage.

Lewkowitzsch (52) tried to prepare nitro fatty acids by direct nitration. He treated caproic acid with nitric acid under conditions which would probably allow the least oxidation to occur. Using nitric acid of specific gravity 1.485 and also 1.550 he allowed the acid to react at room temperature. He also used a mixture of these acids with concentrated sulfuric acid at room temperature and also at slightly elevated temperatures. In no case did he isolate products other than unchanged caproic acid.

- (50) Champion and Pellet, Bull. soc. chim., [37] 24, 449 (1875).
- (51) Badolifte and Polychronis, J. Soc. Dyers Colourists, 36, 65 (1920).
- (52) Lewkowitzsch, J. prakt. Chem., 20, 159 (1874).

carbon dioxide, and oxalic acid. Stearic acid with concentrated nitric acid gave only carbon dioxide, unchanged stearic acid, a small amount of oily fatty acid material, oxalic acid, and sebacic acid. In summarizing the investigations carried out prior to 1879 on the preparation of nitro fatty acids, Lewkowitsch stated that although a series of experiments had been made on the preparation of these compounds, the existence of nitro fatty acids had not been proved through any of the data existing at that time. The work of Dessaigne (47) on nitrovaleric acid was uncertain inasmuch as analyses showed that the product could have been either nitrovaleric or nitroangelic acid. A mixture of products was obtained by Wirtz (53) when coconut oil was treated with nitric acid. The reaction product was found to consist of a mixture of dibasic acids as well as a mixture of nitrocaproic and nitrocapric acids. In further studies he showed that the action of nitric acid on fats produces a mixture of dibasic acids (including oxalic, malonic, succinic, glutaric, adipic, suberic, azelaic and sebacic). All other investigators of this subject prior to 1879 (46,48) agree that fatty acids are oxidized to shorter chain acids and dibasic acids with nitric acid. The later work of Claus and Pfeiffer (49) shows that nitrogen may also be introduced into the fatty acid molecule by this treatment.

Nitro fatty acids have reportedly been prepared from ketones through the action of nitric acid. Chancel (54) heated dipropyl ketone with

(53) Wirtz, Ann., 104, 294 (1857).

(54) Chancel, Ann., 52, 295 (1844); 54, 331 (1848).

ordinary nitric acid and obtained an oily liquid which he identified first as nitrobutyric acid and later as nitropropionic acid. Nitrovaleric acid was obtained as an oily liquid by Brazier and Gossleth (55) from the action of nitric acid on diamyl ketone. Kurtz (56) showed that nitropropionic acid could be formed from dipropyl ketone. His data differ from those of Chancel, however. The work of Schmidt (57) is more positive. He treated dipropyl ketone, dibutyl ketone, and diamyl ketone with nitric acid and obtained nitropropionic, nitrobutyric, and nitrovaleric acid, respectively, as well as oxidation products.

The nitration of esters has been used to prepare -nitro acids. Steinkopf and Supan (58) treated diethyl isosuccinate with fuming nitric acid in acetic anhydride to form diethyl nitro-isosuccinate which was hydrolyzed and decarboxylated to -nitropropionic acid. -Nitroisobutyric acid was prepared by these workers using a similar method. -Nitropropionic acid melts with decomposition at 61° and its salts explode when heated. -Nitroisobutyric acid melts at 93-94°. There is much confusion in the literature regarding the properties of -nitro acids, and it appears that they are quite unstable. Kolbe (59) treated chloroacetic acid with potassium nitrite and obtained nitromethane instead of the -nitro acid. This procedure is a very good one for the preparation of nitromethane. Lowkowitzsch (52) tried to prepare -nitroacetic acid and -nitropropionic acid by treating the corresponding -iodo acids with silver nitrite but

(55) Brazier and Gossleth, Ann., 75, 262 (1850).

(56) Kurtz, ibid., 161, 208 (1872).

(57) Schmidt, Ber., 5, 597 (1872).

(58) Steinkopf and Supan, ibid., 43, 3239 (1910); 44, 2891 (1911).

(59) Kolbe, J. prakt. Chem., [2], 5, 427 (1872).

was unable to isolate any of the desired products. However, when l-iodo-propionic acid was treated with silver nitrite the l-nitropropionic acid was obtained. This was reduced to l-alanine.

Auger (60) showed that Kolbe's method of preparing nitromethane from chloroacetic acid could be extended to the preparation of certain higher nitroparaffins. By using a modification of Kolbe's technique he was able to obtain nitroethane from α-bromopropionic acid (50% yield), nitropropane from α-bromobutyric acid (45% yield), and nitrohexane from α-bromoheptylic acid (35% yield). He was unable to prepare nitropentadecane from α-bromopalmitic acid using this method. In no case did he isolate the intermediate nitro acids, which apparently were readily decomposed with the steam used in distilling the nitroparaffins.

Menke (61) has run a series of interesting nitrations on malonic ester. When fuming nitric acid was used, the product was mononitromalonic ester. With either concentrated nitric acid in acetic anhydride or copper nitrate in the same medium the product was dinitromalonic ester. If copper nitrate in acetic acid was used as the nitrating agent, the product was the mononitro compound.

The most promising results that have been obtained in nitrating aliphatic compounds have been obtained with the hydrocarbons themselves. Konowalow (62) nitrated both normal- and branched-chained hydrocarbons by

(60) Auger, Bull. soc. chim. Paris, 37 25, 333 (1900).

(61) Menke, Rec. trav. chim., 40, 361 (1911).

(62) Konowalow, Ber., 29, 2199 (1896); 26, 1852 (1895); J. Chem. Soc., 92, 1 (1907); J. Russ. Phys. Chem. Soc., 25, 472 (1893); 28, 109 (1900).

heating them with dilute nitric acid in sealed tubes. n-Hexane yielded 50% of a mononitration product, and 2,5-dimethylhexane and 2,7-dimethyl-octane each gave a mixture of mono- and dinitration products. Using dilute nitric acid, Konowalow was able to nitrate side chains attached to benzene. In each case the nitro group entered on the carbon atom attached to the phenyl group. Worstall (63) used fuming nitric acid to nitrate hexane, heptane, octane, nonane and decane to mixtures of mono- and dinitrated products. The yields were 40% or less of nitro compounds, the remainder of the hydrocarbons being oxidized to carbon dioxide, acetic acid, oxalic acid and succinic acid. In 1936, Haas and co-workers (45) published the results of their studies on the vapor phase nitration of gaseous hydrocarbons. The vapors of the hydrocarbons and of nitric acid were passed rapidly through a hot reaction zone and the products condensed and fractionated. The process is now being used commercially to produce the lower nitroparaffins and owes its success in part to the efficient fractionating systems that are used to separate the mixtures of nitrated products that are formed. The reaction probably involves the formation of free radicals. This has been shown by the fact that all of the possible products that may theoretically be formed from the free radicals predictable by loss of a hydrogen atom or by fission of a carbon-carbon linkage in n-pentane have actually been isolated from the nitration of this hydrocarbon (64). Although vapor phase reactions are feasible with comparatively low-boiling compounds they become less practical as the molecular weight increases.

(63) Worstall, Am. Chem. J., 20, 202 (1898); 21, 210, 218 (1899).

(64) McCleary and Degering, Ind. Eng. Chem., 30, 64 (1938).

and, in the case of long-chained fatty acids, it is doubtful that such a method can be employed, owing to the high boiling points of these substances. It seems, therefore, that the nitration of long-chained compounds must necessarily be carried out in the liquid phase and that the problem of inhibiting accompanying oxidation under these conditions must be dealt with.

Sulfur Compounds

A number of long-chained compounds containing sulfur have found use in commerce. Perhaps the most important of these at the present time are the sulfuric acid esters of long-chained alcohols. The sodium salts of these esters are well known as excellent detergents, surpassing the ordinary soaps in some particulars. Dodecyl thiocyanate finds use as a contact insecticide and exhibits properties that make it superior to many plant extractives that are used for this purpose (65). The germicidal properties of the salts of α -mercapto- and α -disulfido-fatty acids of high-molecular-weight have suggested the use of these as germicidal soaps (66). Octadecyl xanthate may be used as a rubber vulcanization accelerator and also has properties that make it suitable as a flotation, wetting, or penetrating agent (67). N^1 -n-Dodecanoylsulfanilamide has been found to be equal to or slightly superior to sulfanilamide in the treatment of beta hemolytic streptococcal infections in mice (68). The fat-solubility of

(65) Bousquet, Salzberg and Dietz, Ind. Eng. Chem., 27, 1342 (1935).

(66) Eggerth, J. Exp. Med., 53, 27 (1931).

(67) U. S. Patent 2,037, 717 [C. A., 30, 3835 (1936)].

(68) Crossley, Northey and Hultquist, J. Am. Chem. Soc., 61, 2950 (1939).

this compound has suggested its probable use in combating human tuberculosis. It has been argued that such a fat-soluble substance could penetrate the tubercle of the causative organism and be effective against the disease.

The successful application of many long-chained sulfur compounds already known serves as an impetus for the preparation and investigation of other long-chained sulfur types.

1. Sulfides, Sulfoxides and Sulfones of High-Molecular Weight

It is surprising that only one of the symmetrical n -alkyl thio ethers above octyl has been described in the literature. Cetyl sulfide was prepared by Fridau in 1852 from potassium hydrosulfide and cetyl chloride (69). The corresponding sulfoxide and sulfone were not prepared, however. The patent literature (70) mentions the production of aliphatic sulfides from inorganic sulfides and alkyl halides of ten to fifteen carbon atoms, but their description appears to have been withheld. No reference is given to the corresponding sulfoxides and sulfones. von Pieverling attempted to prepare melliloyl (C_{31}) sulfide but obtained the mercaptan instead (71).

A number of long-chained unsymmetrically substituted sulfides was prepared by Jones and Reid (72) by the addition of mercaptans to unsaturated hydrocarbons. The structures of the products were proved by synthesis of the corresponding compounds from the potassium salts of

(69) Fridau, Ann., 53, 16 (1852).

(70) U. S. Patent 2,085, 452 [C. A., 31, 5812 (1937)].

(71) von Pieverling, Ann., 183, 349 (1876).

(72) Jones and Reid, J. Am. Chem. Soc., 60, 2452 (1938).

mercaptans and the normal alkyl halides.

The conversion of thio ethers to the corresponding sulfoxides and sulfones generally proceeds very smoothly, and by proper selection of oxidizing agents either the sulfone or the intermediate sulfoxide may be easily isolated. For instance, Grabowsky (73) treated butyl sulfide with dilute nitric acid and obtained the sulfoxide. When fuming nitric acid was used, butyl sulfone was the product. Hinsberg (74) treated a number of sulfides and disulfides with the calculated quantities of hydrogen peroxide in acetic acid and was able to obtain the corresponding sulfoxides and disulfoxides. Hydrogen peroxide in acetone solution was used by Casdar and Smiles (75) to produce sulfoxides. These investigators concur with Hinsberg in the observation that oxidation of sulfides with hydrogen peroxide may be readily controlled at ordinary temperature so as to proceed only to the sulfoxide stage. Excess peroxide at elevated temperature yields sulfones. Chromic acid in acetic acid is declared by Knoll (76) to be an excellent reagent for the oxidation of sulfides to sulfoxides. The experience of the author has shown that in the presence of a considerable excess of chromic acid sulfones may also be produced. Moist chlorine or bromine have been used by Fries and Vogt (77) to form sulfoxides. The intermediate thio ether dichloride or dibromide is first formed and this

(73) Grabowsky, Ann., 175, 348 (1875).

(74) Hinsberg, Ber., 41, 2836 (1908).

(75) Casdar and Smiles, J. Chem. Soc., 93, 1834 (1906).

(76) Knoll, J. prakt. Chem., 113, 40 (1926).

(77) Fries and Vogt, Ann., 381, 533 (1911).

then undergoes hydrolysis to the sulfoxide.

The more vigorous oxidizing agents bring about the formation of sulfones. The use of fuming nitric acid has been mentioned. Bost and co-workers (78) prepared long-chained alkyl 2,4-dinitrophenyl thio ethers and oxidized these to sulfones, using potassium permanganate in acid solution. Sodium hypochlorite solution has been used in the preparation of aliphatic and aromatic sulfones (79). This reagent appears to be best adapted to the oxidation of alkyl sulfides below heptyl. Benzoyl peroxide is a suitable oxidizing agent for the quantitative formation of both aromatic and aliphatic sulfones (80). Electrolytic oxidation has been used by Fichter and Sjöstedtⁿ to convert certain sulfides to sulfoxides and sulfones (81).

A recent paper by the author (82) describes the preparation and properties of the even-chained symmetrical thio ethers from n-dodecyl to n-octadecyl, as well as the corresponding sulfoxides and sulfones. These compounds are being tested for insecticidal activity.

II. Long-chained Sulfonal-type Compounds

Moyst (83) has reviewed the physiological action of long-chained compounds and has pointed out that there are a number of these that

(78) Bost, Turner and Norton, J. Am. Chem. Soc., 54, 1985 (1932).

(79) Wood and Travis, J. Am. Chem. Soc., 50, 1226 (1928).

(80) Lewin, J. prakt. Chem., 118, 282 (1928).

(81) Fichter and Sjöstedtⁿ, Ber., 43, 3422 (1910).

(82) Hunter, Iowa State Coll. J. Sci., 15, 215 (1941).

(83) Ref. (16), p. 51. 15

exhibit definite physiological activity. The polymethylenimines of Ruzicka (84) such as pentadecanemethylenimine, for example, have strong persistent local anesthetic action. The antistreptococcal action of N¹-n-dodecanoylsulfanilamide has been discussed (p. 28). Chaulmoogric acid, which has met with considerable therapeutic interest as an active agent for the treatment of leprosy (85) is a long-chained carboxylic acid derivative of cyclopentane, and Adams and co-workers (86) have investigated the bactericidal properties of a number of long-chained compounds designed as substitutes for chaulmoogra oils. Both cyclohexyl-substituted long-chained acids having eleven and twelve carbon atoms in the chain and dialkyl acetic acids having fifteen or sixteen carbons in the alkyl chains were found to be among the compound most effective in vitro.

In spite of the water-insolubility of the long-chained compounds, it is evident that many do exert definite physiological action and that the synthesis of certain other long-chained types may produce other substances of physiological and therapeutic interest.

Sulfonal has long been used as a soporific. It was first prepared by Baumann in 1886 by oxidation of the mercaptol resulting from the condensation of ethyl mercaptan and acetone (87).



- (84) Ruzicka, Salomon and Meyer, Helv. Chim. Acta., 20, 109 (1937).
- (85) Karrer, "Organic Chemistry", Nordmann Publishing Co., New York (1936) p. 609.
- (86) Stanley, Coleman, Greer, Sacks and Adams, J. Pharmacol., 45, 149 (1932).
- (87) Baumann, Ber., 19, 2808 (1886).

A number of homologs of sulfonal were synthesized by the same investigator by varying both the ketone and the mercaptan. Staffer (88) applied the method to the preparation of sulfonal derivatives having isopropyl, isobutyl, and isocanyl groups attached to the sulfur atom. Baumann and Kast (89) found that the compound having the strongest soporific action on dogs was the tetraethyl derivative (tetronal). Compounds containing alkyl groups larger than ethyl were not tested by these workers. Derivatives of higher molecular weight than those prepared by Staffer do not appear in the literature with the exception of a compound reported by Thoms (90) in which one of the methyl groups of sulfonal was replaced by the n-nonyl group. The physiological action of this compound was not studied.

The synthesis of long-chained mercaptols was undertaken in this work in order that the chemical and physiological characteristics of these and the derived sulfones might be investigated.

III. Sulfonation of Fatty Acids and Nitriles

The very limited solubility of long-chained compounds in water has been mentioned. This property imposes great limitations on the applicability of these substances. The introduction of solubilizing groups into such molecules would greatly enhance their usefulness and value, and in recognition of this fact the problem of introducing water-solubilizing groups into long-chained fatty acids and nitriles was undertaken by the author.

(88) Staffer, Ber., 23, 3226 (1890).

(89) Baumann and Kast, Z. physiol. Chem., 14, 52 (1890).

(90) Thoms, Ber. deut. pharm. Ges., 11, 3 (1901). Chem. Zentr., 72, [1] 524 (1901).

The carboxyl group on long-chained fatty acids makes possible the water-soluble soaps, the importance of which requires no discussion here. Another solubilizing group of great importance is the sulfonic acid group. Direct sulfonation of aromatic compounds has been widely used to bring about the property of water-solubility in otherwise insoluble substances. Olefinic linkages such as those occurring in cracked petroleum distillates are susceptible to the action of sulfuric acid and may be converted to water-soluble compounds by this reagent. With these unsaturated molecules as well as with those occurring in natural fats and oils the reaction is usually one of sulfation rather than sulfonation. The latter process implies the direct introduction of the sulfonic acid group to form a true sulfonic acid containing a carbon-sulfur linkage, whereas the former (sulfation) denotes the introduction of a sulfate group (OSO_3H), having an oxygen atom interposed between the carbon and sulfur atoms. Practically, the difference is of little importance as both processes result in the formation of water-soluble compounds. The true sulfonic acids are considerably more resistant to hydrolysis than are the sulfuric esters. A variety of sulfated oils are widely used as detergents, as "cutting" and other machine oils, and as textile assistants. These have often been improperly called "sulfonated oils", a name that is misleading in that only a very small proportion of true sulfonic acids are formed when the unsaturated oils from which they are made are treated with sulfuric acid.

The sulfonic acid group has certain advantages over the carboxyl group as a water-solubilizing group. The so-called "lymopal salts" for example, which are produced when long-chained alcohols are treated with sulfuric acid, are soluble not only as the salts of the alkali metals but

also as the salts of the alkaline earth metals. The long-chained carboxylic acids, however, are precipitated in the presence of salts of the alkaline earths and hence are less effective as detergents in hard water than are the salts of sulfated long-chained alcohols.

As has been suggested above, the presence of hydroxyl groups or unsaturated linkages in long-chained molecules permits a sulfation reaction to occur in the presence of ordinary concentrated sulfuric acid, resulting in the formation of water-soluble substances. In the case of completely saturated aliphatic compounds which do not contain such groups, however, it is necessary that sulfonating agents considerably stronger than concentrated sulfuric acid be used. Such reagents as fuming sulfuric acid, chlorosulfonic acid and sulfur trioxide are not only strong sulfonating agents, but usually have a strong oxidizing action. This oxidizing action may introduce complications into the reaction between such agents and long-chained aliphatic compounds. Marked decomposition nearly always accompanies the sulfonation, and in addition to the simple exchange of a hydrogen atom for a sulfonic acid group one must expect that the oxidation reaction will produce unsaturation along the chain, thus permitting the sulfation reaction to take place. Also, inasmuch as unsaturation facilitates further oxidation, it is very probable that cleavage will also occur, giving rise to shorter-chained compounds.

Literature references concerning attempts to replace hydrogen atoms with sulfonic acid groups in saturated aliphatic compounds are few. Ordinary concentrated sulfuric acid seems to be incapable of bringing about sulfonation of an aliphatic chain. Thus, Radcliffe and Medofski (91)

(91) Radcliffe and Medofski, J. Soc. Dyers Colourists, 34, 22 (1918).

showed that palmitic and myristic acid are not acted upon by concentrated sulfuric acid. Burton and Robertshaw (92) pointed out that the reagent may bring about decomposition of fatty acids under certain conditions. van Eldik Thieme (93) prepared an addition product of lauric acid and sulfuric acid by heating it with 98.5% sulfuric acid and allowing the mixture to crystallize. The compound was soluble in petroleum ether and was found to consist of one mole of lauric acid to one and one-half moles of sulfuric acid. It broke up into lauric and sulfuric acids upon addition of excess petroleum ether.

The action of fuming sulfuric acid on saturated hydrocarbons has been studied by Worstall (94) who sulfonated n-hexane, n-heptane and n-octane to both mono- and disulfonic acids in the presence of this reagent. A maximum yield of 40% of sulfonated products was obtained, the rest of the hydrocarbon being oxidized. More recently, Burkhardt (95) has investigated the reaction between n-hexane and fuming sulfuric acid, and the results of his experiments indicated that the reaction is considerably more complicated than did the results of Worstall. The following is taken in part from his report (95, p. 2388): "The present investigation has shown that when an excess of n-hexane is stirred vigorously with fuming sulfuric acid (35 or 65% SO₃) at 0-10° for four to five hours, practically the whole of the sulfuric anhydride is used in the reaction that takes place. One mole of

(92) Burton and Robertshaw, "Sulphated Oils", Chemical Publishing Co., New York (1940).

(93) van Eldik Thieme, J. prakt. Chem., 85, 298 (1912).

(94) Worstall, Am. Chem. J., 20, 664 (1898).

(95) Burkhardt, J. Chem. Soc., 2387 (1930).

sulfur dioxide is formed per mole of hydrocarbon attacked, and it is clear that the oxidation of some of the hydrogen of the hydrocarbon is an important part of the reaction, but it is not clear whether this is a primary reaction or whether sulfonation precedes oxidation. The mixed barium salts (30% yield) obtained from the product were partially unsaturated and contained sulfuric ester groups, apparently in the sulfato-sulfonic acids which are formed by the action of fuming sulfuric acid on unsaturated compounds (compare ethionic acid $\begin{matrix} \text{CH}_2-\text{CH}_2 \\ | \quad \quad \quad \backslash \\ \text{SO}_3\text{H} \quad \text{OSO}_3\text{H} \end{matrix}$) from ethylene and fuming sulfuric acid). No crystalline products have been isolated hitherto from the extremely soluble mixture nor from the derived sulfonyl chlorides or amides. The solid barium salts were precipitated and partially fractionated by addition of alcohol to the concentrated aqueous solution. After much fruitless work directed to the isolation of single substances and to the reduction of the complexity of the mixture, the general nature of the products has been deduced from the chemical properties and analysis of the barium salts and sulfonyl chlorides. An estimate of the proportions of the constituents in the mixture was obtained by considering the analytical data for the barium salt and acid chloride from the sulfonic acids remaining after the sulfato groups had been removed by hydrolysis with dilute sulfuric acid. The barium salt of the hydrolyzed product contained two molecular proportions of disulfonate per molecule of monosulfonate. Five per cent of the hexane chains were unsaturated and it appears that about 30% of the chains contained an hydroxyl group. These hydroxyl groups were very largely or entirely in the form of sulfuric esters in the first product."

Fuming sulfuric acid has marked oxidizing action on the normal fatty

acids, but under proper conditions sulfonation may occur. Melsens (96) treated acetic acid with excess fuming (Nordhausen) sulfuric acid and found that the products were carbon dioxide and sulfur dioxide. He showed that when the reaction was interrupted by the addition of barium carbonate a sulfur-containing organic salt could be obtained. This barium salt, as well as the salts of lead, silver, iron, mercury, calcium, etc., was soluble in water and crystallized with varying proportions of water depending upon conditions. The free acid was very hygroscopic.

Chlorosulfonic acid acts on both acetic and butyric acids to give sulfonated organic acids (97).

According to the patent literature, acids such as stearic and palmitic may be sulfonated by oleum, sulfur trioxide or chlorosulfonic acid to form wetting and emulsifying agents (98). In some procedures, organic solvents such as aromatic hydrocarbons or indifferent compounds such as α, β -dichloroethane, carbon tetrachloride, or trichloroethylene are used in the reaction (99). In all such references there is no discussion concerning the chemical structure of the products and little information can be gained regarding the nature of the reaction that takes place.

Oxygenated aliphatic compounds are quite easily charred by oxidizing agents such as fuming sulfuric acid and it has been considered that perhaps less difficulty would be encountered if the substance chosen for the

(96) Melsens, Ann., 52, 275 (1844).

(97) Baumstark, ibid., 140, 81 (1866).

(98) U. S. Patent 1,926,442 [C. A., 27, 6001 (1933)]7,
U. S. Patent 1,939,169 [ibid., 28, 1479 (1934)]7.

(99) German Patent 583,686 [ibid., 28, 1212 (1934)]7,
French Patent 773,656 [ibid., 29, 1436 (1935)]7.

experiments contained no oxygen. Stearonitrile is such a compound, and the aliphatic nitrile group shows remarkable stability, as has been shown by the fact that stearonitrile may actually be cracked to yield lower molecular weight nitriles (100). However, inasmuch as stearonitrile is readily hydrolyzed to the amide in the presence of concentrated sulfuric acid and as an oxygen atom has been introduced into the molecule by this treatment, perhaps nothing is to be gained in starting with the nitrile rather than the amide or even with stearic acid itself.

Several attempts to sulfonate long-chained aliphatic compounds have been made in these laboratories. Hoyt (101) tried to sulfonate tri-n-octadecylamine by treating it with acetic anhydride and concentrated sulfuric acid, with acetic anhydride and fuming sulfuric acid, and with 20% oleum but in all cases was unable to isolate sulfur-containing organic products. That the aliphatic chain in p-phenoxystearophenone can be sulfonated was shown by McCorkle (102) who treated this compound with chlorosulfonic acid and obtained a trisulfonic acid, which, upon oxidation, gave 4-sulfo-4'-biphenylcarboxylic acid, indicating that two of the sulfonic acid groups were located on the aliphatic side chain.

(100) Ralston, Harwood and Poole, J. Am. Chem. Soc., 59, 986 (1937);
Ralston, Selby and Poole, Ind. Eng. Chem., 33, 682 (1941);
Ralston, Christensen, Hoffman, Selby and Conquest, Nat'l. Petroleum News, 28, No. 50, 59 (1936).

(101) Ref. (16), p. 127.

(102) McCorkle, Doctoral Dissertation, Iowa State College (1938), p. 76.

EXPERIMENTAL

Nitrogen Compounds

I. Carboxylic Acid Salts and Amides of n-Dodecylamine and n-Octadecyl-amine.

A. n-Dodecylamine Derivatives.

1. Preparation of N-n-Dodecylammonium Acetate, n-C₁₂H₂₅NH₃COOCH₃
(103). Six-tenths gram (0.01 mole) of glacial acetic acid and 1.85 g. (0.01 mole) of n-dodecylamine were heated to boiling in petroleum ether (b.p. 60-68°), filtered, and allowed to cool. The precipitated salt weighed 2.2 g. (90%) and melted at 67-68° upon recrystallization from the same solvent.

Anal. Calcd. for C₁₄H₃₁O₂N: N, 5.71. Found: N, 5.54.

2. Preparation of N-n-Dodecylacetamide, n-C₁₂H₂₅NHCOCH₃ (104).

One gram of N-n-dodecylammonium acetate was placed in a 50 cc. Erlenmeyer flask through which a slow stream of nitrogen was passed. The flask was heated in a Wood's metal bath at 250° for ten minutes, during which time water was smoothly evolved. The presence of the nitrogen gas excluded oxygen and prevented discoloration of the product. The material which solidified on cooling weighed 0.9 g. (90%) and melted at 53-54°

(103) This salt has been described by Ralston (2).

(104) Prepared previously by other methods (11,14).

after recrystallization from petroleum ether (b.p. 60-68°).

Anal. Calcd. for $C_{14}H_{29}ON$: N, 6.15. Found: N, 5.85.

3. Preparation of *N-n*-Dodecylammonium Stearate, $n-C_{12}H_{25}NH_3^+OOC-$
 $n-C_{17}H_{35}$. Stearic acid (2.85 g., 0.01 mole) and *n*-dodecylamine (1.85 g., 0.01 mole) were dissolved in hot petroleum ether and allowed to cool. The salt was filtered from the cold solution and dried. The product weighed 4.45 g. (95%) and melted at 69-70°. Recrystallization from petroleum ether failed to raise the melting point.

Anal. Calcd. for $C_{30}H_{63}O_2N$: N, 2.93. Found: N, 2.93.

4. Preparation of *N-n*-Dodecylstearate, $n-C_{12}H_{25}NHCO_2C_{17}H_{35}$.

This amide was prepared by heating 1 g. of *N-n*-dodecylammonium stearate for fifteen minutes at 225-250° in an atmosphere of nitrogen. The product weighed 0.85 g. (85%) and melted at 85-85.5° after recrystallization from petroleum ether. A mixture of this compound with the product obtained by Harber (105) from the direct pyrolysis of equimolar quantities of stearic acid and *n*-dodecylamine melted at 85-85.5°.

B. *n*-Octadecylamine Derivatives.

1. Preparation of *N-n*-Octadecylammonium α -Pyrate, $n-C_{18}H_{37}NH_3^+$

$OOOC_4^2O$. One-hundredth mole (2.69 g.) of *n*-octadecylamine was dissolved in 150 cc. of warm petroleum ether and 1.12 g. (0.01 mole) of redistilled α -furoic acid added to the warm solution. The reactants completely dissolved, and upon slow cooling, 5.60 g. (95%) of the white crystalline salt deposited. The melting point (91-92°) was not changed

(105) Melting point sample kindly provided by W. I. Harber (11).

on recrystallization from petroleum ether.

Anal. Calcd. for $C_{28}H_{43}O_2N$: N, 3.57. Found: N, 3.56.

2. Preparation of N - n -Octadecyl- α -furoamide, n - $C_{18}H_{37}NHCOOC_4H_9O$.

a. By Pyrolysis of N - n -Octadecylammonium α -Furoate. Two and one-half grams of N - n -octadecylammonium α -furoate was heated to 275° for twenty minutes in an atmosphere of nitrogen. The product was obtained as a solid on cooling, and weighed 2.3 g. (92%). The melting point of the crude material (77 - 78.5°) was raised to 79.5 - 80.5° upon recrystallization from petroleum ether.

Anal. Calcd. for $C_{28}H_{41}O_2N$: N, 3.60. Found: N, 3.91.

b. From n -Octadecylamine and α -Furoyl Chloride. Five-hundredths

mole (13.5 g.) of n -octadecylamine was suspended in 50 cc. of 10% sodium hydroxide solution. The mixture was constantly shaken while 9.5 g. (0.075 mole) of α -furoyl chloride (106) was added in small portions. Upon cooling, the amide solidified. The alkaline solution was decanted and the solid was washed several times with water and finally melted and resolidified in successive portions of water. The dried material was recrystallized from 95% alcohol and a quantitative yield (18.1 g.) of the amide was obtained. The melting point of 79.5 - 80.5° was unchanged on subsequent recrystallizations from alcohol. A mixture of this product with that obtained in (a) above melted at 80 - 80.5° .

3. Preparation of N - n -Octadecylammonium Benzoate, n - $C_{18}H_{37}NH_2COOC_6H_5$.

(106) Prepared according to directions of Gilman and Hewlett, Iowa State Coll. J. Sci., 4, 29 (1930).

This salt was formed by warming 2.69 g. (0.01 mole) of n-octadecylamine and 1.22 g. (0.01 mole) of benzoic acid in 100 cc. of petroleum ether. The product crystallized from the cooled solution and weighed 3.7 g. (95%). This melted at 63-65°, and after a single recrystallization from petroleum ether melted sharply at 65-66°.

Anal. Calcd. for $C_{25}H_{43}O_2N$: N, 3.59. Found: N, 3.45.

4. Preparation of N-n-Octadecylbenzamide, $n-C_{18}H_{37}NHCOC_6H_5$ (107).

a. By Pyrolysis of N-n-Octadecylammonium Benzoate. Two and four-tenths grams of N-n-octadecylammonium benzoate was heated to 300° for ten minutes in the presence of nitrogen. After evolution of water was complete, the product was cooled and allowed to solidify. It weighed 2.25 g. (95%), and after recrystallization from petroleum ether melted at 85-86°.

b. From n-Octadecylamine and Benzoyl Chloride. An authentic sample of N-n-octadecylbenzamide was prepared from 2.69 g. (0.01 mole) of n-octadecylamine in 30 cc. of 10% sodium hydroxide solution by treating with 3.0 g. (100% excess) of benzoyl chloride. Four grams of crude material was obtained from the cooled reaction product after thorough washing with water. This was recrystallized from petroleum ether and 2.8 g. (75%) of pure product was obtained which melted at 85.5-86°. A mixture of this substance with that obtained by pyrolysis of N-n-octadecylammonium benzoate melted at 85.5-86°.

5. Preparation of N-n-Octadecylammonium α -Naphthoate, $n-C_{18}H_{37}NH_3^+$

$OCOC_{10}H_7^-$. This salt was prepared by warming 2.69 g. (0.01 mole) (107) This amide has been prepared previously (11,18).

of n-octadecylamine with 1.72 g. (0.01 mole) of α -naphthoic acid in 100 cc. of petroleum ether. The product was filtered from the cooled solution and recrystallized from the same solvent. Four grams (92%) of pure material was obtained that melted at 108-110°.

Anal. Calcd. for $C_{29}H_{47}O_2N$: N, 3.17. Found: N, 3.14.

6. Preparation of N-n-Octadecyl- α -naphthamide, $n-C_{18}H_{37}NHCOO-C_{10}H_7$.

a. By Pyrolysis of N-n-Octadecylammonium α -Naphthoate. Two grams of the salt was heated in a stream of nitrogen gas at 250° for fifteen minutes. The cooled product weighed 1.7 g. (87%) and melted at 89-90° after recrystallization from petroleum ether.

Anal. Calcd. for $C_{29}H_{45}ON$: N, 3.32. Found: N, 3.48.

b. From n-Octadecylamine and α -Naphthoyl Chloride. Three-hundredths mole (5.7 g.) of α -naphthoyl chloride (from α -naphthoic acid and thionyl chloride) was added to 3.4 g. (0.02 mole) of n-octadecylamine suspended in 30 cc. of 10% sodium hydroxide solution. The mixture was agitated during the addition of the acid chloride. The crude product (8.7 g.) was washed very well with several portions of hot water and was recrystallized once from acetone and once from methyl alcohol. The purified product weighed 6.0 g. (72%) and melted at 88-89°. A mixture of this material with the product from the pyrolysis of N-n-octadecylammonium α -naphthoate melted at 89-90°.

7. Preparation of N-n-Octadecylammonium Nicotinate,

$\text{n-C}_{18}\text{H}_{37}\text{NH}_2 \cdot \text{C}_5\text{H}_4\text{N}_2\text{O}_2$ (108). One-hundredth mole (2.69 g.) of n-octadecylamine and 1.23 g. (0.01 mole) of nicotinic acid were warmed together in 50 cc. of petroleum ether. The solution was filtered from a small amount of undissolved nicotinic acid, and from the cooled filtrate 2.1 g. (54%) of the salt deposited. After recrystallization from petroleum ether, the compound melted constantly at 78-79°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{44}\text{O}_2\text{N}_2$: N, 3.74. Found: N, 3.50.

8. Preparation of N-n-Octadecylnicotinamide, n-C₁₈H₃₇NHCOC₅H₄N.

One-tenth gram of N-n-octadecylammonium nicotinate was converted to the amide by heating at 250° for ten minutes. The product, after recrystallization from alcohol, weighed 0.08 g. (80%) and melted at 91-92°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{42}\text{ON}_2$: N, 3.74. Found: N, 3.90.

II. Long-chained Pyrrole Derivatives.

A. Preparation from Mucic Acid.

1. Preparation of N-n-Octadecylpyrrole, n-C₁₈H₃₇NC₄H₄. Two-hundredths mole (5.4 g.) of n-octadecylamine and 0.02 mole (4.2 g.) of mucic acid were placed in a 125 cc. Erlenmeyer flask. The mixture was heated in a nitrogen atmosphere at 210° in a Wood's metal bath. Carbon dioxide and water were evolved, and after one hour the

(108) This salt was used to identify the carbonated reaction product prepared by S. M. Spatz (unpublished work) from 3-bromopyridine and n-butyllithium. This product was converted to the n-octadecylammonium salt and a mixed melting point determination showed that the material was identical with that prepared in this experiment.

reaction was completed. The cooled product was warmed with 10% sodium hydroxide solution, cooled, filtered and washed well with water. The dark product was recrystallized from alcohol to yield 5.0 g. (78%) of a brown powder which melted at 73-75°. In spite of the color, the material appeared to be quite pure, and five recrystallizations changed the melting point very little. The product from this treatment melted at 74-75° and was light tan in color.

Anal. Calcd. for $C_{22}H_{41}N$: N, 4.38. Found: N, 4.45, 4.63.

B. Compounds Derived from Acetonylacetonone.

1. Preparation of 1-n-Octadecyl-2,5-dimethylpyrrole, $\bar{n}-C_{18}H_{37}$

$NC_4H_9(CH_2)_2$. One-hundredth mole each of \bar{n} -octadecylamine (2.69 g.) and acetonylacetonone (1.20 g.) were mixed in a 50 cc. Erlenmeyer flask and warmed on a steam bath. The reaction started immediately and water was evolved. The flask was finally warmed carefully on a hot plate for a few minutes to complete the reaction. The product crystallized upon cooling and weighed 3.5 g. (quantitative yield). After recrystallization from alcohol the compound melted constantly at 39-40°. It was observed that the colorless plates gradually changed to a reddish color when exposed to the air. The pure colorless material was analyzed.

Anal. Calcd. for $C_{18}H_{45}N$: N, 4.04. Found: N, 4.02, 4.18.

2. Preparation of 1-n-Dodecyl-2,5-dimethylpyrrole, $\bar{n}-C_{12}H_{25}NC_4H_9$

$(CH_3)_2$. One-tenth mole each of \bar{n} -dodecylamine (18.5 g.) and acetonylacetonone (12.0 g.) were placed in a small Claisen distilling flask and warmed on a water bath for thirty minutes. The flask was then cautiously warmed with a free flame until the water was removed. The

residual oil was then distilled under diminished pressure. Twenty-one grams (79%) of product was obtained which boiled between 138-140° at

1 mm. pressure: d_{25}^{25} 0.86874, n_D^{25} 1.4760, M_D (calcd.) 84.2, M_D (obsd.)

85.2. The substance was a clear, colorless oil which gradually became yellow upon standing and became dark when exposed to the atmosphere.

Anal. Calcd. for $C_{18}H_{33}N$: N, 5.33. Found: N, 5.48, 5.30.

C. Compounds Derived from Diethyl Diacetosuccinate.

1. Preparation of 1-n-Octadecyl-2,5-dimethyl-3,4-dicarboethoxy-

pyrrole, $n-C_{18}H_{37}NC_4(CH_3)_2(COOC_2H_5)_2$. Diethyl diacetosuccinate was prepared from ethyl acetoacetate by the method of Knorr and Haber (109). To 5.16 g. (0.02 mole) of this keto ester was added 5.40 g. (0.02 mole) of n-octadecylamine. The mixture was warmed to 150° for fifteen minutes and the evolved water was largely eliminated at this temperature. The cooled product weighed 10 g. (quantitative yield) and slowly crystallized upon standing at 4°. Upon recrystallization from 80 cc. of alcohol the compound melted at 33-33.5°. The material appeared to be quite stable in air.

Anal. Calcd. for $C_{30}H_{53}O_4N$: N, 2.85. Found: N, 3.13.

2. Preparation of 1-n-Octadecyl-2,5-dimethyl-3,4-dicarboxypyrrole.

$n-C_{18}H_{37}NC_4(CH_3)_2(COOH)_2$. Four grams of 1-n-octadecyl-2,5-dimethyl-3,4-dicarboethoxypyrrole was refluxed for three hours with 1 g. of potassium hydroxide in 30 cc. of alcohol. The mixture was poured into water, filtered, and the filtrate acidified. The crude product weighed

(109) Knorr and Haber, Ber., 27, 1155 (1894).

3.6 g. This material was recrystallized from dilute acetone and melted slightly at 80-95°. It was apparent that the ester had not been completely hydrolyzed. It was redissolved in 30 cc. of alcohol and refluxed with 1 g. of potassium hydroxide for five hours. The solution was diluted with water and part of the alcohol was evaporated off. The solution was cooled and acidified, whereupon the product separated. After two recrystallizations from dilute acetone the compound melted at 107-108° and weighed 1 g. (28%). The substance was not decomposed by exposure to the atmosphere.

Anal. Calcd. for $C_{26}H_{46}O_4$: N, 3.22. Found: N, 3.26, 3.23.

3. Preparation of 1-n-Dodecyl-2,5-dimethyl-3,4-dicarboethoxy-

pyrrole, $n-C_{12}H_{25}N_4(CH_3)_2(COO_2H_5)_2$. Two-hundredths mole

each of diethyl dicarboxosuccinate (5.16 g.) and *n*-dodecylamine (3.70 g.) were mixed in a small Claisen flask. The reaction began immediately and perceptible warming occurred. The material was warmed under vacuum to complete the reaction and to remove the water that was formed. Finally, the product was distilled under diminished pressure. Six and one-tenth grams (72%) of fluorescent oil was obtained at 240-243° at 0.5 mm. pressure; d_{20}^{20} 0.99412, n_D^{20} 1.4905, n_D (calcd.) 119.5, n_D (obsd.) 118.5. The substance was differentially distilled, and the product obtained was slightly contaminated with dark decomposition products which affected the analysis reported here. Hydrolysis of the material, however, yielded the corresponding di-acid (see preparation of this below) and left no doubt as to the structure of the oil.

Anal. Calcd. for $C_{24}H_{41}O_4$: OC_2H_5 , 22.0. Found: OC_2H_5 , 21.0, 21.0

4. Preparation of 1-n-Dodecyl-2,6-dimethyl-3,4-dicarboxypyrrole.

$\text{H}-\text{C}_{12}\text{H}_{25}\text{NC}_4(\text{CH}_3)_2(\text{COOH})_2$. Two grams of 1-n-dodecyl-2,6-dimethyl-3,4-dicarboethoxypyrrole was added to a solution of 0.5 g. of potassium hydroxide in 30 cc. of alcohol. The reactants were refluxed for four hours and then diluted with two volumes of water. The mixture did not form a clear solution, and therefore heating was again applied to the diluted solution and continued for eight hours. The clear solution that resulted was acidified, whereupon 2 g. of crude product was obtained which melted at 85-93°. Recrystallization from dilute acetone (four times) yielded 0.5 g. (30%) of colorless crystals melting at 96-97°. The compound was stable in air.

Anal. Calcd. for $\text{C}_{20}\text{H}_{33}\text{O}_4\text{N}$: N, 3.99. Found: N, 4.00, 3.92.

III. The Action of Nitrous Acid on n-Dodecylamine.

A. First Experiment (Preliminary). One-half mole (92.5 g.) of n-dodecylamine was placed in a large beaker, cooled in ice, and 250 cc. of six normal hydrochloric acid (1.5 moles) gradually added. The mixture was well stirred as a solution of 104 g. (1.5 moles) of sodium nitrite in 200 cc. of water was slowly added. Nitrogen was copiously evolved. After the evolution of gas had subsided, the beaker was removed from the ice bath, allowed to warm up to room temperature, and finally heated nearly to boiling and allowed to cool. The layers were separated and the organic layer taken up in ether. The aqueous layer was extracted twice with ether and the combined extracts added to the ether solution of the main product. The ether solution was washed well with water and dried over sodium sulfate. The solvent was evaporated off and the residual oil (70 g.) fractionated in an electrically heated column. Table II

Table II

Fractionation (First Experiment)

Fraction	Wt. %	$\frac{D}{20}$	Microso	Tests	Halogen	Uranium
(a) 78°/15mm.	9.5	26	neg.	neg.	pos.	pos.
(b) 65-103/15mm.	2.0	1.4332	"	slight	slight	slight
(c) 108-110 / "	7.5	1.4382	slight	pos.	neg.	neg.
(d) 111-114 / "	12.0	1.4391	pos.	"	"	"
(e) 108-109 / 8mm.	10.0	1.4382	"	"	"	"
(f) 110-118 / "	7.5	1.4398	"	"	"	"
(g) 121-124 / "	6.0	1.4406	"	"	"	"
(h) 124-130 / "	5.0	1.4421	"	"	"	"
Residue	10.0					
Total Recovery	66.5					

Table III

Fractionation (Second Experiment)

Fraction	Wt. %	$\frac{D}{20}$	$\frac{D}{20}$	Formic
(1) 74-75°/15mm.	7.0	18	1.4312	0.7634 unseparated
(2) 80-108 / "	1.5	3	1.4270	
(3) 108-110 / "	6.0		1.4410	0.8476 Mol. ref. 58.3
(4) 110-118 / "	8.0	47	1.4410	0.8471 " " 58.3
(5) 132-138 / 16mm.	2.5		1.4418	
(6) 136-138 / "	10.0		1.4416	0.8410 " " 58.4
Residue	16.0	30		
Total Recovery	48.0			

summarizes the results of this fractionation and gives the results of tests for the nitroso group (Liebermann), halogen (Beilstein), and for unsaturation (bromine).

The ten grams of residue that remained from the fractionation was placed in a small flask and distilled at five millimeters pressure. Three grams of distillate was obtained which boiled at 230-235°. This material solidified on cooling, and after three recrystallizations from petroleum ether melted consistently at 76-76.5°. The three grams of dark residue that remained undistilled was dissolved in warm petroleum ether and 1 g. of solid separated on cooling. After several recrystallizations from petroleum ether, this product also melted at 76-76.5° (compare with product obtained in B.).

In Table II it will be observed that nearly all fractions gave both positive halogen and nitroso tests. It was therefore considered that insufficient precaution had been taken to preclude the possibility of both hydrochloric and nitrous acids being present in the distilled oil. A second run was made.

B. Second Experiment. The same quantities of materials were used as in the previous experiment. Greater care was taken in maintaining a temperature of near 0° during the course of addition of the nitric solution to the amine hydrochloride. After evolution of nitrogen in the cold had ceased, the temperature was allowed to slowly rise and the mixture was finally heated nearly to boiling. Upon cooling, the organic layer was taken up in ether and washed twice with hydrochloric acid (2 N) (to remove any unreacted dodecylamine) and then twice with dilute sodium

chloride solution. The subsequent drying over potassium carbonate served also to remove any hydrochloric or nitrous acid present. The solution was filtered and the ether distilled off. The 77 g. of residual oil that remained was well cooled, whereupon a quantity of solid material separated out. This was filtered from the oil, and after removing as much oil as possible on a suction filter the solid weighed 13 g. However, considerable oil appeared to be occluded, and after several recrystallizations from petroleum ether (b.p. 60-66°), 2 g. of pure substance was obtained which melted at 76-76.5°. Mixed melting point determinations showed that this product was identical with that obtained from the high-boiling oil and also from the final residue in the first experiment (see page 51).

The various fractions of the distilled material (see Table III) were examined:

Fraction (1) gave a distinct test for unsaturation with bromine in carbon tetrachloride and has physical properties which agree with those of n-dodecene-1. The material was converted to 1,2-dibromododecane:

1. Preparation of 1,2-Dibromododecane (110). Five grams (.0298 mole) of n-dodecene-1 was dissolved in 50 cc. of carbon tetrachloride. To this was gradually added an accurately measured amount of exactly 10% solution of bromine in carbon tetrachloride. The end point was indicated by the appearance of a slight color of bromine which remained after standing for ten minutes. The theoretical amount (.03 mole) of bromine was taken up from the 48 cc. of 10% bromine solution that was required. The solution was washed with dilute sodium bisulfite solution and then dried over

(110) Prepared previously by Krafft, Ber., 17, 1371 (1884). The constants were not reported.

calcium chloride. After removal of the solvent the residue was distilled. A fore-run of 1 g. of material boiling below 156° at 6 mm. was taken. Pure 1,2-dibromododecane was then distilled off, 5.5 g. (60%) being recovered between $156-158^{\circ}$ at 6 mm.: d_{20}^{20} 1.2315, n_D^{20} 1.4880 (110). M_p (calcd. for $C_{12}H_{24}Br_2$) 73.1, M_p (obsd.) 73.7.

Fraction (2), representing 3% of the oil, was a mixture of n-dodecene-1 with a small amount of higher boiling material.

Fractions (3), (4), (5) and (6) all had very nearly the same refractive indices and densities. The values of 58.3 and 58.4 that were obtained for the molecular refractions are in agreement with that calculated for n-dodecanol (58.8). The three larger fractions, (3), (4) and (6), were each converted to α -naphthyl-n-dodecylurethane by the following general procedure (III):

2. Preparation of α -Naphthyl-n-dodecylurethane. One gram of n-dodecanol was placed in a test tube and 0.5 cc. of α -naphthyl isocyanate added. The solution was warmed on a steam bath for ten minutes, cooled, and allowed to crystallize. The product was recrystallized from petroleum ether (b.p. $60-68^{\circ}$) and melted at $76-77^{\circ}$.

Mixed melting point determinations showed that the urethanes prepared from fractions (3), (4), and (6) were each identical with one another and with an authentic sample of α -naphthyl-n-dodecylurethane prepared from Eastman's n-dodecanol. Inasmuch as the distillation of the various fractions was conducted at varying pressures, it is not particularly significant that the boiling points of the several fractions show considerable variation.

(III) Pickel and French, J. Am. Chem. Soc., 48, 747 (1926).

Fraction (6) appeared to be contaminated with a substance which reacted positively to the Liebermann nitroso test. Assuming the contaminant to be didodecylnitrosamine, the following test was performed: One cc. of the oil was saturated with dry hydrogen chloride. Four cubic centimeters of ether was added and the mixture allowed to stand until fine needles separated out. These melted at 101-101.5° and weighed 0.07 g. (3.5% of the oil). This product was not the expected didodecylamine hydrochloride, which melts at 207-208° (112). The small amount of material was not further investigated.

Fractions (3), (4), (5), and (6) all reacted positively to Beilstein's halogen test, but gave only a faint indication of halogen on fusion with sodium. It is not unlikely that small amounts of n-dodecyl chloride were present.

Fraction (7) was a high-boiling residue which solidified on cooling. The dark product was recrystallized several times from petroleum ether (b.p. 60-68°) whereupon 2 g. of solid melting at 76-76.5° was obtained. A mixed melting point determination with the initial precipitate from the original reaction product showed that these two substances were identical. It also was observed that when the similar high-boiling residue from the first experiment (A) was distilled, a product was obtained which boiled at 230-235° at 5 mm. and which melted at 76-76.5° after recrystallization from petroleum ether. This material also proved to be identical with the above product. Nitrogen analyses gave the following values for this substance: Damas, 4.00, 4.12, 3.95; Kjeldahl, 3.83. These values are much too low to agree with that required by didodecylnitrosamine (7.33% N)

(112) Wojcik and Adams, J. Am. Chem. Soc., 56, 2419 (1934).

which is the product assumed to be present in the high-boiling residue from the comparative studies of Whitmore (35) on n-butylamine. The product was not altered when boiled with concentrated hydrochloric acid. An attempt was made to reduce the material by refluxing for two hours with tin and concentrated hydrochloric acid. The original material was recovered unchanged.

IV. Nitration of Lauric Acid.

A. Action of Dilute Nitric Acid on Lauric Acid. Twenty grams (0.1 mole) of lauric acid was placed in an all-glass apparatus consisting of a three-necked flask, reflux condenser, mechanical stirrer and glass stopper. To this was added 250 cc. of nitric acid (sp. gr. 1.075) (from 13.5 cc. of concentrated nitric acid diluted to 1000 cc.). The mixture was stirred and heated at 125° for twenty hours. The organic layer was separated and washed several times with hot water and allowed to cool, whereupon the material became solid. Upon drying, the product weighed 20 g. and was found to have the same melting point as the original lauric acid. A mixed melting point with lauric acid gave no depression.

B. Action of Concentrated Nitric Acid on Lauric Acid. One hundred grams (0.5 mole) of lauric acid and 100 cc. of concentrated nitric acid (sp. gr. 1.42) were placed in the nitrating apparatus and heated without stirring for ten hours. The layers were allowed to separate and the aqueous layer removed. Concentrated nitric acid (100 cc.) was again added and the heating continued for twenty-four hours. The aqueous layer was removed again and 100 cc. more of concentrated nitric acid was added. Heating was

resumed for twenty-four hours. The mixture was then poured into water and the oil separated and washed several times with hot water. Only 20 g. of material remained undissolved. This residual oil had a specific gravity greater than that of water. The rest of the initial organic material was apparently oxidized to carbon dioxide and water-soluble substances. Evaporation of the combined aqueous layers and washings yielded a slushy mass which was separated into 40 g. of white crystalline material (probably dibasic acids) and 20 g. of oily residue which contained a considerable amount of nitric acid. These products indicate that under these conditions oxidation is the predominant reaction.

C. Action of Fuming Nitric Acid on Lauric Acid in the Cold. Lauric acid (90 g.) and 100 cc. of fuming nitric acid (sp. gr. 1.50) were mixed and stirred in the nitrating apparatus. Marked cooling of the mixture occurred as the lauric acid dissolved, and the temperature of the solution fell to 10° C. By means of a water bath the temperature was maintained between 10 and 15° overnight. The solution was then poured into water and the organic layer separated. This was washed four times with water and dried. Unchanged lauric acid was quantitatively recovered. It was purified by dissolving in sodium hydroxide solution, reprecipitating the acid with hydrochloric acid and recrystallizing the dried product from acetone. A mixed melting point with lauric acid showed no depression.

D. Nitration of Lauric Acid with Fuming Nitric Acid at Reflux Temperature.

1. First Experiment. One hundred grams (0.5 mole) of lauric acid was placed in the nitrating apparatus with 100 cc. of fuming nitric acid.

The temperature was gradually increased until the nitric acid refluxed gently. Large volumes of gases were evolved and these were passed through sulfuric acid and then over lime water. The sulfuric acid served to remove the oxides of nitrogen and the lime water showed that carbon dioxide was being given off in large quantities.

The mixture was refluxed with stirring for seven hours and 100 cc. more of fuming nitric acid was added. The reaction was allowed to continue for seventeen hours longer and the mixture was then poured into water. The oily layer was separated and washed several times with hot water and finally taken up in ether and dried over sodium sulfate. After removal of the ether the residual oil weighed 52 g. This slowly became buttery in consistency on standing. In an attempt to steam-distill this product no organic matter was carried over with one liter of distillate. The oil was once again taken up in ether and dried over sodium sulfate. The ether was removed and 50 cc. of 95% ethyl alcohol was added to the residual oil. On good cooling a small amount of solid material separated. This was filtered off and recrystallized several times from acetone. The purified product melted at 43-44° and a mixed melting point determination with lauric acid showed no depression. The alcohol was distilled from the remaining oil and the residue was placed in an extraction apparatus and extracted with petroleum ether (b.p. 60-68°). The volume of the oil was diminished by half. The undissolved oil was warmed in an evacuated flask to remove traces of solvent and was then analyzed.

Anal. Calcd. for $C_{11}H_{23}NO_2$: N, 6.98. Found: N, 6.39, 6.95.

Later experiments have shown that the product from the above treatment is a mixture and the analyses are therefore of questionable value.

They prove, however, that nitrogen has been definitely introduced into the lauric acid. A sodium fusion test also definitely showed the presence of nitrogen in this material. The nitrated oil was soluble in 10% sodium hydroxide solution, giving a yellow color. Upon acidification, the yellow color was dispelled in the solution and an oil separated out on the surface which changed from a yellow to green color on standing.

The petroleum ether solution containing the dissolved portion of the original oil was distilled to remove the solvent and 20 c. of residual oil remained. Absolute ethyl alcohol (100 cc.) was added to this product and the mixture was saturated with dry hydrogen chloride. After nine hours at room temperature the solution was poured into water. The organic layer was separated, washed well with water, then with dilute sodium hydroxide solution, and finally several times with water. That the material had been esterified was shown by the fact that it was now insoluble in 10% sodium hydroxide solution in contrast to the unesterified product. A few drops of the ester were added to a test tube containing a solution of sodium in alcohol. The oil immediately dissolved, forming a clear yellow solution. Upon acidification with dilute hydrochloric acid, a green oil separated which retained the nut-like odor characteristic of the ester. The color changes noticed in these tests are indicative of the presence of an aliphatic nitro group. The original nitrated product, as well as the esterified material, was yellow in color.

2. Second Experiment. Lauric acid (150 g., 0.75 mole) was mixed with 150 cc. of fuming nitric acid and refluxed with stirring for twenty-four hours. The mixture was poured into water and the oil layer removed

and washed several times with hot water. The product was taken up in ether, dried over sodium sulfate, and the solvent removed. The yield of oil was 77.5 g. (51% of the starting material). Upon standing overnight 3 g. of white solid separated out. This was filtered off and recrystallized from dilute alcohol. The material melted sluggishly between 38 and 43° and probably was impure lauric acid (see previous experiment). The filtered oil was extracted with petroleum ether (to remove unreacted lauric acid). About one-half of the material had dissolved in the solvent. The remaining undissolved oil was then heated in a vacuum to remove residual solvent and 20 g. of the oil was obtained. In order to check the previous experiment, this material was analyzed. A low nitrogen value was obtained (4.06% N). Five grams of the oil was dissolved in 50 cc. of alcohol and to this was added a solution of 0.57 g. of sodium in 50 cc. of alcohol to which 50 cc. of petroleum ether had been added. A yellow salt precipitated which was filtered off and washed well with petroleum ether. After thorough drying the product weighed 2.0 g.

One-half gram of the above sodium salt was dissolved in water and lead acetate solution added until no further precipitate formed. The slightly yellow salt was filtered off and washed well with water, alcohol, acetone, alcohol again, petroleum ether, and finally with ether. Three grams of lead salt was obtained which appeared to be insoluble in water and all organic solvents tried. The compound was analyzed for nitrogen and for lead (113).

(113) The procedure used in the lead analysis was that of Gilman and Robinson, J. Am. Chem. Soc., 50, 1714 (1928).

Anal. Calcd. for $(C_{10}H_{21}CH_2COO)_2Pb$: N, 4.6; Pb, 34.05.
" " $(C_{10}H_{21}CH(NO_2)COO)_2Pb$: N, 4.04; Pb, 29.8.
" " $C_{10}H_{21}C(NO_2)COOPb$: N, 3.12; Pb, 46.0.

Found: N, 2.29, 2.32; Pb, 42.5.

The salt was probably impure despite the careful washing with five solvents listed.

The petroleum ether extract of the original oil was evaporated until free from solvent and after standing overnight the oil was filtered from a small amount of separated solid material (lauric acid). The filtered oil weighed 30 g. Five grams of this material was dissolved in alcohol and added to 0.94 g. of sodium in the same solvent. The precipitated salt weighed 2.7 g. and was converted to the lead salt by dissolving in water and adding lead acetate solution. The lead salt was carefully washed with water, alcohol, petroleum ether, and ether, and after thorough drying, was analyzed for lead. Anal: Found: Pb, 58.0, 58.8. These values do not check the theoretical possibilities listed above nor do they check the value for lead laurate (Pb, 33.3). The high percentage of lead suggests the presence of other lead salts in the material.

3. Third Experiment. One mole (200 g.) of lauric acid was placed in the all-glass nitrating apparatus with 200 cc. of fuming nitric acid. The mixture was gently refluxed without stirring for eighteen hours. The lower aqueous layer was removed and the oil replaced in the apparatus with 100 cc. more of fuming nitric acid. Heating was resumed for another eighteen hours. Fuming nitric acid (100 cc.) was again added and the mixture heated for twenty-five hours longer. The mixture was poured into water and the

organic layer separated and washed well with hot water and then dried over sodium sulfate. The filtered oil (47 g.), representing 24% of the starting material, was then distilled at 3 mm. pressure to give the following fractions:

(1)	70-80°	2.5 g.
(2)	80-90	3.0
(3)	90-130	3.0
(4)	150-180	1.0
(5)	180-185	5.0
(6)	185-195	<u>25.0</u>
Recovery		39.5 g. (84%)

Between fractions (3) and (4) violent foaming took place (bath temperature of 150-160°). After thirty minutes of very cautious heating, the foaming gradually subsided and a yellow liquid distilled off, giving fractions (4), (5), and (6). Fraction (6) was redistilled at approximately 0.5 mm. and 18 g. of clear yellow oil was obtained boiling between 163-166° (mostly at 165-166°); d_{25}^{25} 1.0441, n_D^{25} 1.4572. Two possible structures seemed worthy of consideration: (a) $C_{10}H_{21}CH(NO_2)COOH$ (nitrododecanoic acid); and (b) $C_{11}H_{23}NO_2$ (nitroundecane). The following quantitative data were obtained on the yellow oil:

Anal. Calcd. for (a): N, 5.83; Calcd. for (b): N, 6.96.

Found: N, 4.59, 4.78, 4.75.

Neut. equiv. Calcd. for (a): 245 (carboxyl hydrogen). Calcd. for (b): 201 (aci-form). Found: 191, 191.

Molec. ref. Calcd. for (a): 64.8. Found for (a): 64.0.
Calcd. for (b): 58.9. Found for (b): 52.5.

4. Fourth Experiment. Two moles (400 g.) of lauric acid was warmed to reflux temperature with 200 cc. of fuming nitric acid for twelve hours. The aqueous layer was removed and 200 cc. more of the fuming nitric acid added. After refluxing for twelve hours more, the aqueous layer was again removed and 200 cc. of fresh fuming acid added. The boiling was continued for eighteen hours. The layers were separated and the oil was washed with hot water eight times. The residual oil weighed 142 g. (35% of the original lauric acid). Upon washing with hot water five times more, the weight of the oil was reduced to 123 g. This was distilled at 1 mm. pressure to give the following fractions:

(1)	80-120°	10.5 g.
(2)	120-140	5.0
(3)	140-150	2.0
(4)	150-170	5.5
(5)	170-180	6.5
(6)	180-200	<u>46.0</u>
	Recovery	77.5 g. (63%)

Considerable decomposed material could not be distilled and remained as a charred mass in the distilling flask.

Fraction (1) was redistilled at atmospheric pressure. A small amount of distillate was collected at 180-195° and the bulk of the material boiled off at 195-200° (750 mm.). Neutralization equivalent determinations on the latter fraction gave the following values: 111.0, 110.5. Pure caproic acid boils at 199.5-200° at 750 mm. and has a neutralization equivalent of 116.0.

Fraction (6) was washed repeatedly (ten times) with hot water until

the washings remained clear on cooling. Seventeen grams of oil remained. This was washed five times more with hot water and then dried over sodium sulfate. The 13 g. of oil that was obtained was distilled once more and 10 g. of product was recovered, boiling between 195-200° at 1 mm. pressure. This was analyzed for nitrogen. Anal. Found: N, 4.70, 4.72. These values agree with those obtained in the Third Experiment but are too low for nitrododecanoic acid or for nitroundecane.

The oil was redistilled and analyzed once more. Anal. Found: N, 4.64. The oil was definitely acidic and three neutralization equivalent determinations each gave the value of 225.0.

The following tests were applied to the oil:

(a) Attempted Reduction. Two grams of the nitro oil (b.p. 195-200°/1 mm.) was placed in a small acetylating flask and 2 g. of tin metal (granular) was added. A solution of 2 cc. of concentrated hydrochloric acid in 2 cc. of water was added and the mixture warmed gently for six hours. Small additions of dilute hydrochloric acid were made periodically. The mixture was cooled and poured into a flask containing 10% sodium hydroxide solution. The odor of ammonia was detected and a piece of litmus paper held over the mouth of the flask turned blue. The alkaline mixture was warmed and upon cooling was extracted with ether. The ether extract was dried over sodium sulfate and then saturated with dry hydrogen chloride. No precipitation occurred. Evaporation of the ether left only a trace of organic matter. The alkaline stannate solution was acidified with hydrochloric acid and extracted with ether. After washing and drying, the ether was removed and 1.5 g. of yellow oil was recovered.

Similarly, attempted reductions with iron in acetic acid and with zinc

in hydrochloric acid yielded no basic organic matter.

(b) Action of Alcohol and Dry Hydrogen Chloride. Five drops of the nitro oil were placed in a test tube and 3 cc. of alcohol added. Dry hydrogen chloride was passed slowly through the solution for five hours. No precipitate was observed. One-half of the alcohol was evaporated off and hydrogen chloride was passed through the remaining solution for ten hours. No precipitate was formed. Water (5 cc.) was added and the layers separated. The aqueous solution was tested for hydroxylamine hydrochloride with Fehling's solution. No reduction was observed. Nitromethane, under corresponding conditions, gave hydroxylamine hydrochloride crystals and the aqueous extract reduced Fehling's solution immediately.

The combined washings containing the water-soluble portion of fraction (6) were evaporated to dryness and 20 g. of solid material was obtained. Repeated recrystallization from water gave a small amount of crystalline material which melted at 127-128°. A Dumas nitrogen determination showed that the substance was free from nitrogen. Two neutralization equivalent determinations gave the same value of 99.1. These values are in reasonable agreement with those of sebacic acid which melts at 133° and has a neutralization equivalent of 101.2. No derivative was prepared from the small amount of material available.

5. Fifth Experiment. One hundred and fifty grams (0.75 mole) of lauric acid was stirred with 100 cc. of fuming nitric acid for three hours in the cold and then refluxed with stirring for eight hours. Another addition of 100 cc. of fuming nitric acid was made and the refluxing and stirring were continued for thirty-five hours. The oil was poured into

water and the organic layer separated and washed repeatedly with fresh portions of hot water. After drying in ether over sodium sulfate and removal of the ether, 64 g. of oil was obtained. Fifteen grams of this product was distilled at 1 mm. pressure to give the following fractions:

- | | | | |
|-----|---------|------|--------------|
| (1) | 80-105° | 3 g. | (liquid) |
| (2) | 105-130 | 2 | (solid) |
| (3) | 130-150 | 2 | (solid) |
| (4) | 150-170 | 2 | (liquid) |
| (5) | 170-180 | 2 | (semi-solid) |
| (6) | 180-185 | 2 | (solid) |

Fraction (1) corresponded to that identified as caproic acid in the previous experiment.

Fraction (2) melted at 35-43°, and after several recrystallizations from acetone melted at 43-44°. A mixed melting point with lauric acid was not depressed.

Fraction (3) consisted of lauric acid with some higher boiling material.

Fraction (4) was yellow in color and gradually developed into a slushy mass on standing. A few drops of the warmed material dissolved readily in 10% sodium hydroxide solution, giving a distinct yellow color. Upon addition of hydrochloric acid the yellow color was discharged and an oil formed on top of the solution.

Fractions (5) and (6) were not investigated but undoubtedly were the same as the higher boiling material described in earlier experiments.

6. Esterification of Nitrated Lauric Acid Mixture. The remaining 60 g. of undistilled oil from the previous experiment was esterified

with 200 g. of absolute ethyl alcohol by saturating the alcoholic solution with dry hydrogen chloride. After standing for six hours, the mixture was poured into water and the ester separated and washed several times with water, then rapidly with sodium carbonate solution and finally with water. (Although the sodium carbonate washings were colored yellow, only a very small amount of oil separated when the alkaline solution was neutralized). The ester was dried with sodium sulfate overnight and 53 g. of product having a definite ester odor was obtained. This was distilled to give the following fractions at 1 mm. pressure:

(1)	45-50°	4.0 g.
(2)	55-90	4.5
(3)	90-115	11.0
(4)	115-135	10.0
(5)	135-140	5.0
(6)	140-150	<u>9.5</u>
	Recovery	44.0 g.

Fraction (1) had an odor like that of ethyl caproate and distilled at 160-165° at atmospheric pressure. It had a refractive index of 1.4259 at 25°. These constants are in agreement with those recorded for that ester.

Fractions (3) to (6) were redistilled to give the following fractions at 1 mm. pressure:

(a)	106-110°	5.0 g.
(b)	110-115	8.0
(c)	115-130	2.0
(d)	130-140	4.0

(e)	140-150°	6.0 g.
(f)	150-160	<u>10.0</u>
	Recovery	35.0 g.

Fraction (f) was analyzed for nitrogen.

Anal. Calcd. for $C_{10}H_{21}OH(NO_2)COOC_2H_5$: N, 5.13. Found: N, 5.31, 5.27.

The density and refractive index of fraction (f) were determined and found to be 0.98712 and 1.4452 respectively, both measured at 25° C.

M_p (calcd. for $C_{10}H_{21}OH(NO_2)COOC_2H_5$) 74.17, M_p (obsd.) 75.35.

E. Attempted Nitration of Ethyl Laurate. One-half mole (122.5 g.) of pure ethyl laurate (b. p. 144-146°/4mm.) and 100 cc. of fuming nitric acid were placed in an all-glass apparatus consisting of a large flask and a reflux condenser. The reaction began immediately, and with carefully controlled heating was allowed to proceed for seven hours. Unless care was used, the reaction became vigorous and large volumes of gases were evolved. The mixture was allowed to cool and the aqueous layer was separated. Fuming nitric acid (100 cc.) was again added and the reactants carefully heated for twelve hours. The whole of the material was then poured into water and the organic layer separated and washed free from nitric acid with cold water and then washed several times with hot water. The remaining oil (90 g.) represented 73% of the initial ethyl laurate. The product was twice distilled at 3 mm. pressure to give the following fractions:

(1)	62-132°	4 g.	(liquid)
(2)	132-139	33	(solid)
(3)	140-180	5	(semi-solid)
(4)	180-185	14	(liquid)

(5)	185-190°	1 g.	(liquid)
(6)	190-200	3	(solid)
		<hr/>	
	Recovery	60 g.	(66%)

Fraction (1) was similar to the material identified in previous experiments as caproic acid.

Fraction (2), representing over 50% of the recovered material, was lauric acid. This was proved by careful recrystallization of the substance from acetone, whereupon the melting point (43-44°) remained the same when the product was mixed with pure lauric acid.

Fraction (3) was a mixture of lauric acid with some higher boiling material.

Fraction (4) had a refractive index at 25° of 1.4575, which was very close to that observed on the higher-boiling material obtained in the nitration of lauric acid. The color, odor, and solubility behavior also recalled that product.

Fraction (5) melted sluggishly at 92-130° and resembled the similar product that was identified as dibasic acid material in the high-boiling fraction from the nitration of lauric acid.

Sulfur Compounds

I. High-Molecular-Weight Sulfides, Sulfoxides and Sulfones (114)

A. Preliminary Preparations

1. Preparation of Ethyl Stearate. The procedure used was similar

(114) The preparation of only the *n*-octadecyl derivatives is described here. The formation of the *n*-dodecyl, *n*-tetradecyl, and *n*-hexadecyl compounds has been given elsewhere by the author (ref. (82)).

to that described by Hoyt (115). Two hundred and fifty grams (0.88 mole) of pure stearic acid (116) was dissolved in 300 cc. of warm absolute ethyl alcohol and the resulting solution completely saturated with dry hydrogen chloride. After standing at room temperature for six hours, the entire mixture was poured into a large excess of warm water and the ester layer separated and washed several times with warm water. The product was washed with dilute sodium hydroxide solution, taken up with ether, and the ether solution washed several times with water. After drying overnight with sodium sulfate the ether was removed and the residual oil distilled under diminished pressure. Practically all of the material distilled constantly at 190-192° at 4 mm., and 298 g. (90%) of the ester was obtained.

2. Preparation of n-Octadecanol (117). Sixty-five grams (0.2 mole) of ethyl stearate was placed in a 500 cc. bomb of a Parr hydrogenation machine. Six grams of copper-chromium oxides catalyst (118) was added and the bomb filled with hydrogen (1640 lbs. pressure at 25° C.). The temperature was raised to 250° and maintained there for four and one-half hours. After cooling, the product was removed, dissolved in hot acetone, and filtered. Fifty-two grams (94%) of n-octadecanol (m. p. 57-58°) crystallized from the cooled filtrate.

3. Preparation of n-Octadecyl Bromide (119). A mixture of 38 g.

- (115) Hoyt, Doctoral Dissertation, Iowa State College (1940) p. 89.
(116) Pure stearic acid was obtained by recrystallization of Neo-fat 1-65 (kindly provided by Armour and Co.) from acetone.
(117) Ref. (115) p. 90.
(118) Folkers and Connors, J. Am. Chem. Soc., 54, 1138 (1932).
(119) Variations of this procedure have been described by Hoyt (ref. (115) p. 96) and by McCorkle, Doctoral Dissertation, Iowa State College, 1938, p. 85.

of 42% hydrogen bromide and 13 g. of concentrated sulfuric acid was placed in a 250 cc. three-necked flask equipped with a mechanical stirrer and reflux condenser. Twenty-seven grams (0.1 mole) of n-octadecanol was gradually added and the reactants refluxed with stirring for six hours. Another addition of 19 g. of 42% hydrogen bromide was made and the refluxing continued for one hour. The reaction mixture was poured into water, the bromide layer separated, washed with cold concentrated sulfuric acid, then with water, and finally with sodium carbonate solution. The oil was taken up with ether, washed once more with water, and the ether solution dried over sodium sulfate. After removal of the ether (water bath) the bromide distilled at 194-195° at 6 mm. The yield was 30.5 g. (91%).

B. Preparation of n-Octadecyl Sulfide and Its Oxidation Products.

1. Preparation of n-Octadecyl Sulfide (120). Five grams (0.22 g-atom) of sodium metal was dissolved in 200 cc. of absolute ethyl alcohol. The solution was divided into two equal portions; the first part was saturated with dry hydrogen sulfide and to this was added the second half of the sodium ethylate solution. A solution of 26.8 g. (0.08 mole) of n-octadecyl bromide in 200 cc. of absolute alcohol was then added to the alcoholic sodium sulfide solution. The mixture was refluxed for eight hours on a steam bath and was then filtered hot. Upon cooling the filtrate, the sulfide crystallized in the form of lustrous plates. These were filtered off and melted in distilled water. After cooling, the solid was removed and melted as before until the water no longer showed any cloudiness in the presence of the melted sulfide. The product was allowed to dry and when (120) This procedure is a modification of that used by Fridan (ref. (69) for the preparation of n-hexadecyl sulfide.

recrystallized from acetone weighed 16 g. (75%) and melted at 68-69°.

Anal. Calcd. for $C_{36}H_{74}S$: S, 5.94. Found: S, 5.93.
(by Pregl's micro Pearl tube method)

2. Preparation of n-Octadecyl Sulfide.

a. With Chromic Acid in Acetic Acid. One gram (0.00185 mole) of n-octadecyl sulfide was dissolved in 100 cc. of hot glacial acetic acid. To this was added 0.25 g. (0.0025 mole) of chromic acid (CrO_3) in one-half cc. of water and 5 cc. of acetic acid. The brownish-green solution that immediately developed changed to a clear green solution. The mixture was kept warm for two hours, cooled, and the crystals filtered off. Upon recrystallization from acetic acid, these melted at 99-100° and weighed 0.92 g. (92%).

Anal. Calcd. for $C_{36}H_{74}SO$: S, 5.77. Found: S, 5.86, 5.85.

b. With Dilute Nitric Acid. One gram of n-octadecyl sulfide was added to 100 cc. of dilute nitric acid (50 cc. of concentrated nitric acid in 50 cc. of water). The mixture was warmed on a steam bath for thirty minutes, cooled, filtered, and the solid material recrystallized from acetone. The product weighed 0.3 g. (30%) and melted at 99-100°. A mixed melting point with the product of (a) showed no depression.

3. Preparation of n-Octadecyl Sulfone

a. With Hydrogen Peroxide in Acetic Acid. n-Octadecyl sulfide (1.0 g.) was dissolved in 100 cc. of warm glacial acetic acid. Five cubic centimeters of 30% hydrogen peroxide was added and the solution kept warm for four hours. The dried product weighed 0.9 g. (90%) and melted at 105.5-106.5°.

Anal. Calcd. for $C_{36}H_{74}SO_2$: S, 5.61. Found: S, 5.61, 5.58.

b. With Fuming Nitric Acid. One gram of n-octadecyl sulfide was added to 50 cc. of fuming nitric acid and the mixture warmed on a steam bath for one hour. The acid mixture was poured into water, filtered, and the solid recrystallized from acetic acid. One-half gram of product (50% yield) was obtained which melted at 105.5-106.5°. A mixed melting point with the sulfone obtained in (a) was not depressed.

c. With Excess Chromic Acid in Acetic Acid. In an effort to make n-octadecyl sulfoxide from 1.0 g. of the sulfide and 0.25 g. of chromic acid in acetic acid, a product was obtained from one run that melted low (92-96°). This was treated once more with 0.25 g. of chromic acid in acetic acid. The product weighed 1.0 g. and melted sharply at 105.5-106.5°. A mixed melting point with an authentic specimen of n-octadecyl sulfone showed no depression. This is significant inasmuch as Knoll (76) states that even though a moderate excess of chromic acid is used the oxidation of sulfides proceeds only to the sulfoxide stage.

4. Reduction of n-Octadecyl Sulfoxide to n-Octadecyl Sulfide. One-half gram of n-octadecyl sulfoxide was dissolved in 100 cc. of hot acetic acid. Zinc dust (2 g.) was added and the mixture refluxed for ten hours. The solution was filtered and allowed to cool. Silvery plates deposited which melted over a wide range (68-85°). The material was redissolved in acetic acid and refluxed with zinc dust for ten hours more. The hot solution was filtered, cooled, and the crystals filtered off and washed with water. The dried product melted at 68-70° and when mixed with pure n-octadecyl sulfide the melting point was 68-70°. The yield was practically

quantitative.

5. Oxidation of n-Octadecyl Sulfoxide to n-Octadecyl Sulfone.

One-half gram of n-octadecyl sulfoxide was dissolved in 100 cc. of acetic acid and 3 cc. of 30% hydrogen peroxide added. The mixture was warmed for two hours, allowed to cool, and the crystals filtered off. After thorough washing and drying, the sulfone was recovered in quantitative yield and melted at 105.5-106.5°. A mixed melting point with pure n-octadecyl sulfone showed no depression.

6. Attempted Reduction of n-Octadecyl Sulfone. One-half gram of

n-octadecyl sulfone was dissolved in 80 cc. of hot acetic acid. To this was added 3.0 g. of zinc dust and the mixture was refluxed for ten hours. The hot solution was filtered, cooled, and the product filtered off. After washing and drying, the sulfone was quantitatively recovered and melted at 105.5-106.5°. A mixed melting point determination with pure n-octadecyl sulfone showed no depression. These results are in agreement with the generally known fact that sulfones are not reduced by the action of zinc in acids, whereas sulfoxides are reduced to sulfides by this treatment.

II. Attempted Preparation of Long-chained Sulfonal-Type Compounds.

A. Preliminary Preparations

1. Preparation and Proof of Structure of n-Octadecyl Mercaptan.

a. Preparation of n-Octadecyl Mercaptan. The method used was a modification of that of Collin and co-workers (121). Three and one-half grams (0.15 g. atom) of sodium was dissolved in 300 cc. of absolute ethyl alcohol. The solution was saturated with hydrogen sulfide and then placed

(121) Collin, Hilditch, Marsh and McLeod, J. Soc. Chem. Ind., 52, 272T (1935).

in a 500 cc. bottle provided with a tightly-fitted stopper. To the alcoholic sodium hydrosulfide solution was added 37.5 g. (0.11 mole) of n-octadecyl bromide in 75 cc. of absolute alcohol. The stopper was firmly secured and the bottle placed in a steam jacket for ten hours. The reaction product was then poured into water, extracted with ether, and the ether extract washed twice with water and then dried in a nitrogen-filled bottle over sodium sulfate. After removal of the ether the product was distilled under diminished pressure in an atmosphere of nitrogen. The mercaptan boiled at 215-215.5° at 15 mm., 24.5 g. (76% yield) of product being obtained within this temperature range. Twelve grams of material boiling between 210-215° was also recovered. The main fraction solidified when allowed to stand at room temperature in the absence of oxygen. A portion was recrystallized from absolute alcohol and melted sharply at 31°. Inasmuch as this constant does not agree with the melting point of 56° previously assigned to n-octadecyl mercaptan (121), the material was analyzed and subjected to the following rigorous confirmatory experiments.

Anal. Calcd. for $C_{18}H_{38}S$: S, 11.19. Found: S, 11.15 (Pearl tube); 11.31 (Parr bomb)

b. Preparation of Lead n-Octadecyl Mercaptide. A small amount (0.05 g.) of the n-octadecyl mercaptan prepared above was dissolved in 3 cc. of absolute alcohol. An alcoholic solution of lead acetate was added until no more of the yellow lead mercaptide precipitated. This was filtered off and washed on a Büchner funnel with several portions of hot alcohol, then with hot acetone, and finally with warm ether. The material melted sharply at 110-111° in agreement with the value given by Bost and Fore (122).

(122) Bost and Fore, J. Am. Chem. Soc., 59, 2557 (1937).

These workers did not isolate the pure mercaptan but converted the crude product directly to the lead salt.

c. Oxidation of n-Octadecyl Mercaptan to n-Octadecyl Disulfide. Two-tenths of a gram (0.0007 mole) of n-octadecyl mercaptan was dissolved in 10 cc. of warm alcohol. A solution of 0.2 g. of iodine in 20 cc. of alcohol was added gradually and with shaking to the mercaptan solution until the slightest tinge of yellow color remained (9.0 cc. of the iodine solution was required to reach this end point). The slight excess of iodine was destroyed by the addition of a small amount of sodium bisulfite solution and the alcoholic solution was filtered while warm. The product that crystallized out on cooling melted sharply at 62.5° in agreement with the constant given by Collin (121) for n-octadecyl disulfide. The substance weighed 0.15 g. (75% yield). It gave no color with alcoholic lead acetate solution, thus indicating the absence of the mercaptan. The theoretical quantity of iodine required for the oxidation was 0.089 g.; the amount of iodine actually contained in the 9 cc. of iodine solution used was 0.090 g.

d. Reduction of n-Octadecyl Disulfide to n-Octadecyl Mercaptan. Two grams (0.004 mole) of n-octadecyl disulfide was dissolved in 100 cc. of warm acetic acid and the solution placed in a three-necked flask equipped with a reflux condenser and mechanical stirrer. Two grams of zinc dust was added and then 16 cc. of water was gradually dropped into the mixture as it was stirred and heated to gentle reflux. After three hours, the hot solution was filtered and 1.2 g. (60%) of product separated from the well-cooled filtrate. This was extracted several

times with hot dilute hydrochloric acid, then washed with water, and finally taken up with ether and dried over sodium sulfate in a nitrogen-filled bottle. The ether was removed and the residue recrystallized from 5 cc. of acetone. The product melted at 30.5-31.5°. A mixture of this material with pure n-octadecyl mercaptan melted at the same temperature.

2. Preparation of n-Dodecyl Mercaptan. n-Dodecyl mercaptan was prepared by the same method used in the preparation of n-octadecyl mercaptan. Sodium metal (3.5 g., 0.15 g. atom) was dissolved in 300 cc. of absolute alcohol and the mixture saturated with hydrogen sulfide. This was placed in a 500 cc. bottle with a solution of 25 g. (0.1 mole) of n-dodecyl bromide and heated for three hours in a steam jacket. The product was poured into water, taken up in ether, and dried over sodium sulfate under nitrogen. The ether was removed and the product distilled in an atmosphere of nitrogen at 18 mm. pressure. Fifteen grams of constant-boiling material was obtained within the temperature range of 144-145°. This fraction, representing a 75% yield of the mercaptan, was redistilled at 24 mm. and was found to boil between 153-155°. This agrees with the boiling point of n-dodecyl mercaptan at this pressure as reported by Moller and Gordon (123). In order to more definitely establish the identity of the product, a part was converted to n-dodecyl disulfide.

3. Preparation of n-Dodecyl Disulfide. Two grams of n-dodecyl mercaptan (0.01 mole) was converted to the disulfide by the same method used to prepare n-octadecyl disulfide. A 75% yield (1.5 g.) of the product was obtained, melting at 33.5°. Collin (121) gives 32° as the melting point

(123) Moller and Gordon, J. Am. Chem. Soc., 55, 1090 (1933).

of this substance.

B. Attempted Condensation of n-Dodecyl Mercaptan with Acetone.

1. With Hydrogen Chloride Alone. Two grams (0.01 mole) of n-dodecyl mercaptan was dissolved in 2 cc. of acetone. Dry hydrogen chloride was passed through the solution for thirty minutes, whereupon the mixture separated into two layers. The entire mixture was poured into water and the upper layer removed and washed three times with water. The oil was then taken up in ether and dried over calcium chloride. After removal of the ether (steam bath) the oil was distilled under diminished pressure. One gram of material was recovered between 150-155° at 24 mm. which was shown to be unchanged n-dodecyl mercaptan by oxidation with iodine in alcohol to n-dodecyl disulfide (melting point and mixed melting point, 33.5°) and by the formation of the yellow lead mercaptide when lead acetate solution was added to the oil.

2. With Hydrogen Chloride and Zinc Chloride. In a second run, 5 g. (0.025 mole) of n-dodecyl mercaptan was dissolved in 6.0 cc. of acetone and to this was added 2 g. of anhydrous zinc chloride. Dry hydrogen chloride was passed through the solution until it became quite dark red in color. The mixture was poured into water and the oily layer separated and washed well with water. After drying over calcium chloride, the oil weighed 4.5 g. (90% recovery) and was shown to be unchanged n-dodecyl mercaptan. The material gave the yellow mercaptide test with lead acetate and yielded n-dodecyl disulfide when treated with iodine in alcohol.

C. Attempted Reaction between n-Dodecyl Mercaptan and 2,2-Dichloropropane. Four grams (0.02 mole) of n-dodecyl mercaptan was

dissolved in 20 cc. of petroleum ether (b. p. 60-68°) and 0.46 g. (0.02 g. atom) of sodium metal added. The sodium reacted very slowly and the mixture was heated to effect reaction. After cooling, 1.12 g. (0.01 mole) of 2,2-dichloropropane (from acetone and phosphorus pentachloride by the method of Friedel and Ladenberg (124)) was added. After refluxing for five hours, the mixture was cooled, poured into water, and then heated on a steam bath to remove the solvent. The solid that separated (2.5 g.) was remelted under water several times, dried, and recrystallized from acetone. One and seven-tenths grams of pure material was obtained which melted sharply at 40-40.5° and proved to be identical with n-dodecyl sulfide (mixed melting point 40-40.5°) (125).

Anal. Calcd. for $C_{24}H_{50}S$: S, 8.65. Found: S, 8.86.

1. Confirmation of Formation of n-Dodecyl Sulfide. In order to confirm the identity of the product obtained in the reaction immediately above, the following experiments were carried out:

a. Formation of n-Dodecyl Sulfoxide. Following the method used in the preparation of n-octadecyl sulfoxide from n-octadecyl sulfide (126), 0.05 g. of the product from the above reaction between n-dodecyl mercaptan and 2,2-dichloropropane was oxidized to n-dodecyl sulfoxide (m. p. 89.5-90.5°) with dilute nitric acid. The yield was quantitative and a mixed melting point (125) with pure n-dodecyl sulfoxide showed no depression.

(124) Friedel and Ladenberg, Ann., 142, 315 (1867).

(125) The n-dodecyl sulfide, n-dodecyl sulfoxide and n-dodecyl sulfone used in these mixed melting point determinations have been prepared by the author and the description of their preparation appears elsewhere (see ref. (82)).

(126) This Thesis, p. 71 and ref. (82).

b. Formation of n-Dodecyl Sulfone. Using the method described for the preparation of n-octadecyl sulfone from n-octadecyl sulfide (126), 1.0 g. of the n-dodecyl sulfide obtained above was converted to n-dodecyl sulfone by the action of hydrogen peroxide in acetic acid. The oxidized product melted at 94.5-95.5° and when mixed with pure n-dodecyl sulfone (125) the melting point remained the same.

D. Attempted Reaction between n-Dodecyl Mercaptan and Diethyl Dibromomalonate.

1. With Alcoholic Potassium Hydroxide in Air. The experiment was carried out under normal atmospheric conditions, no attempt being made to exclude the oxygen of the air. To 4.0 g. (0.02 mole) of n-dodecyl mercaptan was added a solution of 1.12 g. (0.02 mole) of potassium hydroxide in 20 cc. of absolute alcohol. To this was added 3.2 g. (0.01 mole) of diethyl dibromomalonate (from malonic ester and bromine by the method of Conrad and Brücknerⁿ (127)). An immediate precipitate appeared. The mixture was warmed for twenty minutes and filtered hot from the inorganic salt. Two and seven-tenths grams of long colorless needles crystallized from the well-cooled filtrate. When recrystallized from alcohol these melted sharply at 35.5° and when mixed with pure n-dodecyl disulfide (128) gave no depression in melting point.

2. With Alcoholic Potassium Hydroxide in Nitrogen. In view of the possibility of atmospheric oxygen being responsible for the oxidation of the

(127) Conrad and Brückner, Ber., 24, 3001 (1891).

(128) This Thesis, p. 75.

n-dodecyl mercaptan to n-dodecyl disulfide in the experiment immediately above, the experiment was repeated with the precaution of excluding air by maintaining a nitrogen atmosphere in the apparatus throughout the reaction. The inorganic salt recovered (potassium bromide) weighed 1.87 g. n-Dodecyl disulfide was obtained in 84% of the theoretical yield (5.3 g.) and melted at 32-33°.

3. With Sodium in Petroleum Ether. In a third experiment, the sodium n-dodecyl mercaptide was prepared first by heating a petroleum ether solution of the mercaptan (2.0 g., 0.01 mole) with 0.23 g. (0.01 g. atom) of sodium until the latter had practically disappeared. One and six-tenths grams (0.005 mole) of diethyl dibromomalonate was added and the mixture refluxed for three hours. The cooled product was poured into water and the oily layer separated and dried. Upon recrystallization from alcohol, 0.6 g. of material was obtained which melted at 40-40.5°. A mixed melting point determination with pure n-dodecyl sulfide showed no depression. Three-tenths gram of the substance was oxidized with 3 cc. of 30% hydrogen peroxide in 30 cc. of hot acetic acid. The product obtained in quantitative yield proved to be n-dodecyl sulfone (melting point and mixed melting point 94-95°).

B. Attempted Reaction between n-Dodecyl Mercaptan and Diethyl α -Bromosuccinate. Potassium hydroxide (0.6 g.) was dissolved in alcohol and added to 0.5 cc. of n-dodecyl mercaptan. To this was added 0.5 cc. of diethyl α -bromosuccinate (129). An immediate precipitate formed and the mixture was heated and the solid filtered off. Upon good cooling, a white

(129) kindly provided by R. W. Laeper.

crystalline product was precipitated. This was filtered off and found to melt at 31-32°. After recrystallization from alcohol, the substance melted at 33.5° and when mixed with pure n-dodecyl disulfide no change in melting point was observed.

F. Conversion of n-Dodecyl Mercaptan to n-Dodecyl Sulfide with Sodium in Petroleum Ether. In order to throw light on the mechanism of the formation of n-dodecyl sulfide from n-dodecyl mercaptan under the conditions of the experiments described above in which sodium was allowed to react on the mercaptan in the presence of petroleum ether, the following modification of a described method (130) for the formation of a sodium mercaptide was undertaken. To 2 g. (0.01 mole) of n-dodecyl mercaptan in 20 cc. of petroleum ether (b. p. 60-68°) was added 0.25 g. (0.01 g. atom) of sodium metal. The mixture was heated for three hours, cooled, and the remaining sodium destroyed by adding 10 cc. of alcohol. The product was poured into water and warmed until the organic material separated as an oil. Upon good cooling, the oil solidified. The aqueous layer was decanted and the crystalline material successively melted and solidified in water until the aqueous layer remained clear. The cooled solid was removed and recrystallized several times from absolute alcohol. One gram (50%) of pure material was obtained which melted at 40-41°. The melting point was not depressed when the compound was mixed with pure n-dodecyl sulfide.

Two-tenths grams (0.001 mole) of the sulfide was oxidized with hydrogen peroxide in acetic acid. n-Dodecyl sulfone was obtained in quantitative

(130) Sodium ethyl mercaptide has been prepared by adding the metal to an ether solution of the mercaptan. Classon, J. prakt. Chem., [2] 15, 193 (1877).

yield (m. p. 94.5-95.5°). This material did not depress the melting point of pure n-dodecyl sulfone.

III. Sulfonation of Long-chained Fatty Acids and Nitriles.

A. Attempted Sulfonation of Stearonitrile.

1. Action of Concentrated Sulfuric Acid. Two grams of stearonitrile was added to 10 cc. of concentrated sulfuric acid (sp. gr. 1.84) at room temperature and the mixture was stirred until all had dissolved. The solution was heated on a steam bath for thirty minutes, cooled, and poured into water. The white solid that precipitated was filtered off and recrystallized from acetone until a constant melting point of 107° was obtained. This material proved to be stearamide, and a mixed melting point with an authentic sample of the amide melted at 107°. The yield of pure compound was 1 g. (48%).

2. Action of Concentrated Sulfuric Acid in Acetic Anhydride.

Stearonitrile (5 g.) was added to a mixture of acetic anhydride (8 g.) and concentrated sulfuric acid (4 g.) in a flask equipped with a mechanical stirrer. The mixture was kept at 0° with stirring for two hours and a sample was removed and poured into water. The resulting precipitate was insoluble in water.

The ice bath was replaced by a steam bath and the temperature was kept at 100° for four hours. The mixture was poured into water. The very dark product was still water-insoluble, indicating that sulfonation had not occurred.

3. Action of Chlorosulfonic Acid. Three cubic centimeters of

chlorosulfonic acid was added to 1 g. of stearonitrile in a test tube. The tube was slightly warmed and the reaction started, giving off considerable hydrogen chloride. The mixture became very dark in color and the reaction was allowed to proceed until no more hydrogen chloride was evolved. The dark mass was poured into water and the solidified product appeared to be completely insoluble, indicating that in spite of the evidences of reaction, water-solubilizing sulfonic acid groups had not been introduced under these conditions. Attempts to decolorize and purify the very dark material were unsuccessful.

4. Action of Fuming Sulfuric Acid. Thirty cubic centimeters of fuming sulfuric acid (20% SO₃) was placed in a three-necked flask equipped with a mechanical stirrer and 3 g. (0.011 mole) of stearonitrile was gradually added. The apparatus was partially immersed in an ice bath and the mixture was stirred constantly for six hours. (An attempt was made in one experiment to conduct the reaction at room temperature. The reaction became violent and blew out through the top of a water-cooled condenser). The stirring was interrupted and after standing at room temperature overnight, 10 cc. more of fuming sulfuric acid was added. The mixture was stirred three hours longer and was then poured onto 100 g. of ice. Practically all of the very dark acid mixture dissolved in the melted ice and the resulting solution was filtered, neutralized with barium carbonate, and heated to boiling. A Buchner funnel was employed to filter off the barium sulfate from the hot solution. The filtrate was evaporated nearly to dryness on a hot plate and the drying was cautiously completed. One and two-tenths grams (equivalent to 40% of the stearonitrile) of brown crystalline material remained. This substance would not melt, but charred, leaving a black

residue insoluble in water. The brown substance was easily soluble in water but appeared to be insoluble in ether, alcohol, acetone, benzene, carbon tetrachloride and ethyl acetate. The odor was not unlike that of cinnamon. An attempt was made to rid the material from impurities by redissolving in water and evaporating to incipient crystallization. The method could not be used to purify the substance as no material separated out until practically all of the water had been removed. A sodium fusion test indicated the presence of both nitrogen and sulfur.

Part of the brown substance (0.5 g.) was redissolved in water and neutralized with a saturated solution of sodium carbonate. The insoluble barium carbonate that precipitated was filtered off and the filtrate evaporated to incipient crystallization. Upon standing, a brown salt crystallized (presumably the sodium salt of a sulfonic acid). An attempt to convert this to a sulfonamide through the sulfonyl chloride by successive treatment with phosphorus pentachloride and ammonia was unsuccessful, the resulting product being insoluble in organic solvents and soluble in water.

In another experiment the aqueous solution of the sulfonated nitrile was treated with milk of lime until the solution was barely alkaline to phenolphthalein. The solution was heated to 80° and the calcium sulfate filtered off. The filtrate was evaporated to dryness and the residue dissolved in 50 cc. of water. The filtered solution was treated with saturated sodium carbonate solution until no more calcium carbonate was precipitated. The calcium carbonate was filtered off and the filtrate evaporated to dryness. The dark residue was unchanged after several treatments with animal charcoal and efforts to resolve the substance into recognizable material met with no success.

B. Sulfonation of Stearic Acid.

1. Action of Fuming Sulfuric Acid in Tetrachloroethane. Twenty grams of stearic acid, 50 g. of fuming sulfuric acid (20% SO_3), and 100 cc. of tetrachloroethane were placed in a flask equipped with an efficient stirrer. The mixture was stirred vigorously at ice bath temperature for nine hours and then at room temperature for six days. A separatory funnel was used to separate the two layers and the upper (tetrachloroethane) layer was steam-distilled to remove the solvent. Upon cooling, the residue solidified. This was filtered off and dried. Nineteen grams of material was obtained. Upon a single recrystallization from acetone the product melted at $68.5-69.5^\circ$ and when mixed with pure stearic acid the same melting point was observed. The 19 g. of acid represented a 95% recovery of the starting material.

2. Action of Chlorosulfonic Acid in Carbon Tetrachloride. Twenty grams (0.07 mole) of stearic acid, 18 g. (0.14 mole) of chlorosulfonic acid, and 100 cc. of carbon tetrachloride were placed in a flask and stirred in an ice bath for nine hours and then at room temperature for six days. The mixture was slowly poured into water, whereupon hydrolysis of the chlorosulfonic acid resulted in the formation of heat and the evolution of considerable hydrogen chloride. Upon cooling, crystals were formed. The entire mixture was placed in a large flask and the carbon tetrachloride was steam-distilled off. The residue partly solidified on cooling. The solid was filtered off and the dried product weighed 18.6 g. Upon recrystallization from acetone the material melted at $68.5-69.5^\circ$. A mixture with pure stearic acid melted at the same temperature. The yield represented a

92% recovery of the original stearic acid.

3. Action of Fuming Sulfuric Acid at Room Temperature. Twenty grams of stearic acid was gradually added to 60 cc. of fuming sulfuric acid (20% SO_3) in a flask that was cooled in an ice bath. The mixture was stirred under these conditions for five hours. A small portion of the mixture was removed and was found to be water-insoluble. The ice bath was removed and the stirring continued at room temperature overnight. The dark acid mixture was poured into ice water and after standing for one hour was warmed sufficiently to melt the separated solid. The material that solidified on cooling was removed and washed well with water. The dried product weighed 15 g. Upon recrystallization from acetone this melted at 69-70° and when mixed with pure stearic acid the melting point was not depressed. Seventy-five per cent of the original stearic acid was recovered.

4. Action of Fuming Sulfuric Acid at 50°. Preliminary experiments showed that it was necessary to add the fuming acid very gradually to stearic acid and to keep the mixture cool during the addition. Otherwise, the reaction became uncontrollable and foamed out of the flask.

One mole (284 g.) of stearic acid was placed in a liter three-necked flask equipped with a stirrer. Four hundred cubic centimeters of fuming sulfuric acid (30% SO_3) was very slowly added over a period of two days. The mixture was allowed to stand at room temperature for two days more, after which time the greater part of the stearic acid had passed into solution. The material was cautiously heated to 50° and held at that temperature with stirring for ten hours. After allowing the mixture to

cool to room temperature, the dark mass was poured onto ice. When the ice had melted, the floating solid was melted by warming to 80°. Upon cooling, a very large part of the material solidified. This was removed, washed and recrystallized from acetone. The recovered material was pure stearic acid (m. p. 68-69°) and weighed 225 g. (80%).

The dark aqueous layer, containing the sulfonated portion of the stearic acid, was filtered and neutralized with barium carbonate. The resulting precipitate of barium sulfate was filtered off and the filtrate was evaporated to dryness. Eleven grams of water-soluble black material was obtained. This represented 18% of the stearic acid that was used in the reaction. The crude material was redissolved in a small amount of water. The dark filtered solution was added dropwise to a flask containing 200 cc. of rapidly stirred absolute alcohol. The precipitate was filtered and dried on a suction filter. This was dissolved and precipitated twice more and finally a tan powder was obtained, weighing 9 g. This was analyzed for barium and the analyses are in agreement with that required for the barium salt of mono-sulfonated stearic acid.

Anal. Calcd. for $C_{16}H_{33}CH(SO_2O)COO_2Ba$: Ba, 28.6. Found: Ba, 29.2, 29.0.

DISCUSSION

The essential purposes of these investigations as stated in an introductory paragraph were fourfold: (1) to examine the limits of homology as applied to long-chained nitrogen and sulfur compounds, (2) to investigate the possibilities of new compounds as derivatives for the identification of long-chained molecules, (3) to develop techniques for applying reactions of short-chained aliphatic compounds to long-chained homologs, and (4) to produce new compounds which hold the possibility of becoming commercially useful themselves or which may serve as intermediates for further work toward that end. The aim of this discussion is to point out, where possible, the success or failure of the accomplishment of these objectives.

Before entering upon a discussion of the application of the limits of homology to aliphatic nitrogen and sulfur compounds it seems desirable to clarify the intended meaning of the word "homology". Briefly, the word as defined in a chemical sense by Webster's Dictionary (131) means "the relation existing between the compounds of a series whose successive members possess, in addition to similarity of structure, a regular difference in formula". To be more explicit in denoting the meaning of the word as it is used in this thesis it might be stated that a given member of a homologous series differs from the preceding or succeeding member by a constant difference, CH_2 . Furthermore, it has been considered that branched-chained compounds are not to be placed in the same homologous series with normal straight-chained compounds. This definition is given in contrast to the

(131) Noah Webster, "Webster's New International Dictionary," Second Edition, Unabridged, G. and C. Merriam and Co., Springfield, Mass. (1934) p. 1194.

interpretation of Whitmore (33) who has considered the class of alcohols, regardless of whether they be primary, secondary, or tertiary as belonging to the same homologous series. The application of the phenomenon of homology as applied to high-molecular-weight fatty acid derivatives has been discussed by McCorkle (132) and an excellent resumé of the limits of homology in long-chained aliphatic compounds in general has been given by Hoyt (133). As Kamm has stated (134), "the existence of homology is of fundamental importance for two reasons: (1) the chemical properties of every member of a homologous series are the same; they differ only in the speed of reaction, not in the kind of reaction, and (2) the physical properties of the members of a given homologous series are different". As has been stated, one of the purposes of these investigations has been to discover the extent to which these features of true homology can be carried into the realm of high-molecular-weight aliphatic nitrogen and sulfur compounds.

The first series of compounds that was examined was the n-octadecylamine salts of an extended group of normal fatty acids. Among these prepared were the salts of all the normal acids from formic to caproic and of the even-chained normal acids from caprylic to stearic, inclusive. Each of the acids reacted readily with n-octadecylamine and the conditions required for salt formation were the same for each member of the series. This result was to be expected inasmuch as salt formation is an ionic reaction and there is little change in the ionization constants of the normal fatty acids as the series is ascended. It is of particular interest,

(132) McCorkle, Doctoral Dissertation, Iowa State College (1938).

(133) Hoyt, Doctoral Dissertation, Iowa State College (1940).

(134) Kamm, "Qualitative Organic Analysis", John Wiley and Sons, New York (1938), p. 5.

however, that the conditions required for the formation of the N-substituted amides from the corresponding salts were practically the same for all members of the series studied. This illustrates to an unusual degree the similarity in reaction of the members of this extended homologous series.

The curves obtained by plotting the melting points of the salts and of the amides against the number of carbons in the parent acids (Fig. I) present interesting examples of the change of this physical property with chain length (135). The first member, as usual, is anomalous, but the succeeding members fall on definite curves which exhibit a minimum point at six carbons in the case of the salts and at four to five carbons in the case of the amides. This type of melting point curve is not unusual with long-chained compounds and Robertson (25) has observed similar curves in his studies with a number of amides of these same fatty acids.

The appreciable differences in melting points observed in the series of n-octadecylamine salts of the normal fatty acids suggests the use of these compounds as derivatives for the identification of these and other acids. The salts are easily prepared in very good yields, and upon simple heating are converted to the amides which may be used as confirmatory derivatives. However, as is the case with most compounds containing long aliphatic chains, mixed melting point determinations are of questionable value in proving the identity of these substances. This is true because only very slight depressions are observed when mixtures of contiguous members in a series of such compounds are melted (136).

(135) The greater part of the data in Fig. I has been taken from a paper by the author (26).

(136) Compare with the observations of Gilman and Ford (24), and of Harber (ref. (11) p. 137).

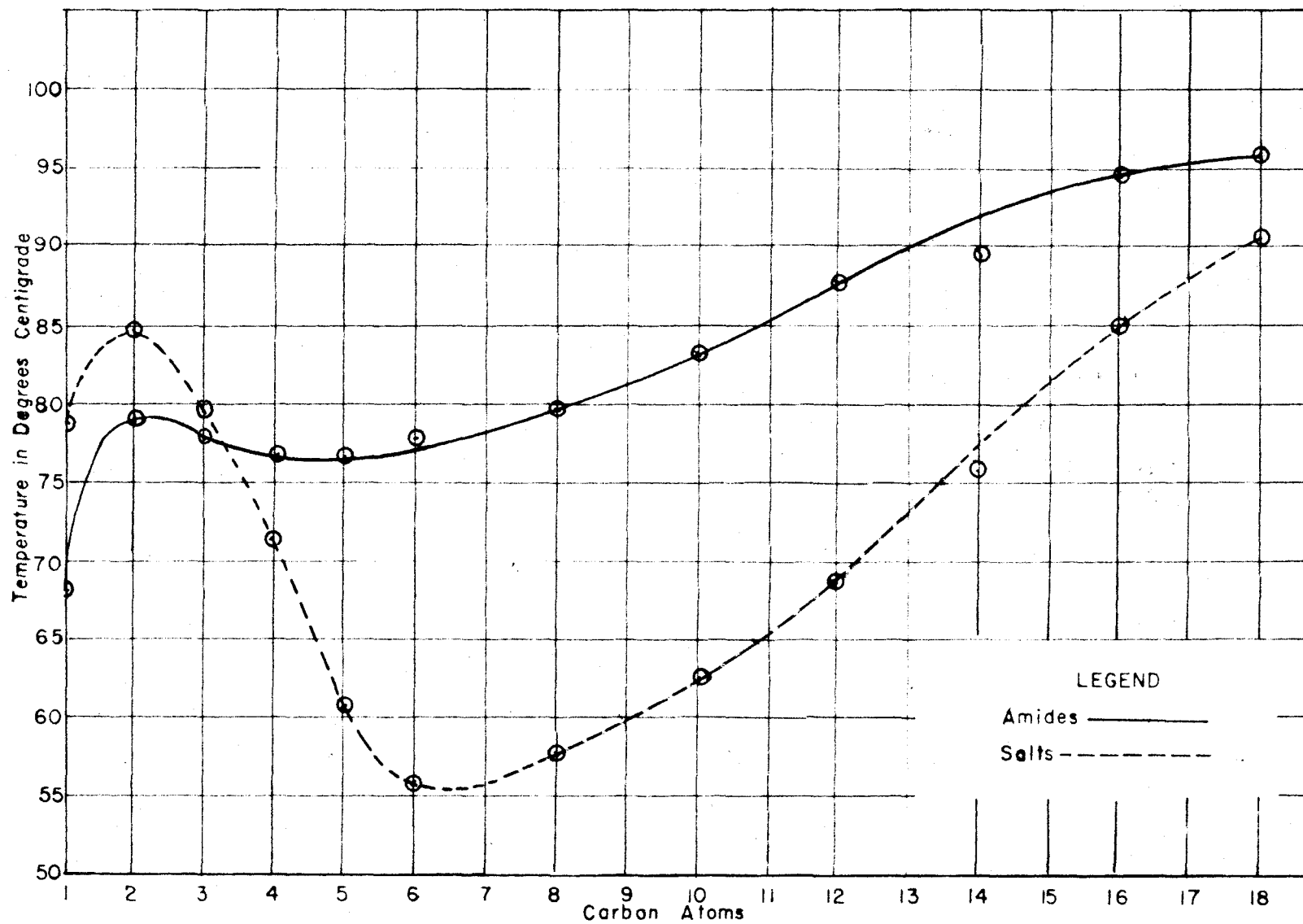


Fig. I. Melting Points of Normal Fatty Acid Salts of *n*-Octadecylamine and Corresponding Amides

It has been mentioned earlier (2) that N-n-dodecylammonium acetate has properties that make it a useful agent for the rapid clarification of turbid waters. Within the wide range of salts prepared in this work it is quite probable that this effect may be more satisfactorily accomplished with one of the compounds listed. The salts are substituted ammonium soaps and their solutions might be expected to demonstrate other useful surface phenomena. Investigations of such phenomena have not as yet been carried out. N,N'-Di-n-octadecylammonium oxalate (26) and N,N'-di-n-dodecylammonium succate (137) both exhibit very interesting lubricating properties. The materials have the unctuous "feel" of talc and might possibly find use as foot powder or as a dusting powder for automobile inner tubes. Certain of the compounds are being tested for insecticidal activity but insufficient data have been obtained at this writing to warrant definite conclusions.

The great ease with which the amine salts of carboxylic acids may be converted to amides provides an excellent method of preparing the amides. The advantages of the method over the procedures that have generally been employed immediately become apparent when one considers that the acid itself, rather than a derivative of the acid, is reacted with the amine. The preparation of such derivatives as acid chlorides, anhydrides, or esters is time-consuming and the yields are not always satisfactory. Furthermore, the yields of amides obtained through the reaction of such derivatives with amines are generally less quantitative than are the yields of pure amides from simple pyrolysis of the amine salts. The isolation of the salts is

(137) Unpublished work by the author.

not essential, and although certain advantages are to be gained by purification of the salt before pyrolysis is applied, good yields of amides have been obtained by Barber (11) by heating equimolar quantities of the acid and amine.

The pyrolysis of the amine salts of mucic and other sugar acids leads to extensive decomposition with the formation of pyrrole derivatives. This reaction was successfully applied to the preparation of N-n-octadecylpyrrole. The product is a crystalline solid which melts at 75°. Similar success was experienced in extending the reaction of 1,4-diketones with amines to form long-chained substituted pyrroles. Thus, acetylacetone reacted with great ease with both n-dodecyl- and n-octadecylamine to form the corresponding N-alkyl-2,5-dimethylpyrroles. The n-octadecyl derivative is a low-melting solid (m. p. 40°) and the n-dodecyl homolog is a liquid which boils at 136-140° at 1 mm. pressure. Both of these compounds are quite unstable in air, and gradually undergo oxidation when exposed to the atmosphere. More stable substances were produced by treating diethyl diacetylsuccinate with each of the two amines. This 1,4-diketone contains esterified carboxyl groups which effectively stabilize the resulting pyrrole derivatives. The reaction of both n-dodecyl- and n-octadecylamine with diethyl diacetylsuccinate proceeds spontaneously on mixing, and appears to be quantitative. This type of reaction, because it is quantitative, is of particular value with long-chained compounds since the problem of separating unreacted material from the products is often difficult in cases where reactions of such compounds do not go to completion. N-n-Octadecyl-2,5-dimethyl-3,4-diaurboethoxypyrrrole, which was produced when n-octadecylamine and diethyl diacetylsuccinate were warmed together, is

a low-melting solid (m. p. 33.5°) which was purified by a single recrystallization from alcohol. The corresponding N-n-dodecyl derivative is a high-boiling liquid (b. p. 240-243°/0.5 mm.) and consequently was less easily purified. Both compounds were hydrolyzed to the corresponding diacids. These acids, as well as the esters, are stable compounds and might well be tested for insecticidal activity in view of the suggested use of lower-molecular-weight pyrrole derivatives for this purpose (32).

The reactions of long-chained amines to form pyrrole derivatives are the same as the similar reactions of the lower-molecular-weight aliphatic amines and again exemplify the principle of homology.

Although the method of preparation of several of the long-chained pyrrole derivatives from amines is simple, the melting points are usually too low for the requirements of good derivatives. The N-alkyl-2,5-dimethyl-3,4-dicarboxypyrroles are considerably higher melting than other pyrrole derivatives described in this work, but they are less easily prepared than are other compounds which may be used for the identification of long-chained amines.

Experiments directed toward the conversion of n-dodecylamine to n-dodecanol by means of nitrous acid gave relatively poor yields (27%) of this alcohol. The reaction product contained large amounts of solid material as well as considerable n-dodecene-1. The solid material yielded a nitrogen-containing substance which was not identified. A small amount of a nitroso compound (possibly dodecyl nitrite) and a halogenated compound (probably dodecyl chloride) were also detected among the products. These results are essentially in agreement with the previously mentioned work of

Whitmore and of Adamson and Kenner (138) who have shown that the reaction of nitrous acid with normal aliphatic amines yields a mixture of alcohols, olefins, and nitrogen-containing bodies. It is particularly significant that only the normal dodecyl alcohol was obtained in the present experiments. This bears out the prediction made earlier and shows that the isomerization observed in the reaction of nitrous acid with amines of lower-molecular-weight becomes insignificant in the corresponding reaction with higher-molecular-weight amines. This should be considered a departure from the more strict concept of homology.

In considering that the main object of investigating the reaction of n-dodecylamine with nitrous acid was to provide a suitable means for converting the amine to the corresponding alcohol it is encouraging to note that the normal alcohol rather than a mixture of isomeric alcohols was formed. However, in view of the fact that other side reactions occur which result in a lowering of the yield of n-dodecanol and in the formation of a considerable proportion of olefins and nitrogen-containing substances it appears that the reaction is of questionable value as a method of preparing n-dodecanol.

Oxidation was the predominant reaction that took place when lauric acid was subjected to the action of nitrating agents. Dilute nitric acid appeared to be incapable of attacking lauric acid, but hot concentrated and fuming nitric acids brought about vigorous decomposition with the formation of carbon dioxide and a mixture of lower-molecular-weight mono- and dibasic acids. Nitrated material was also found in the reaction products. The nature of the oxidation products has previously been determined by other

investigators and the present experiments were confined primarily to the establishment of the structure of the nitrated material. From the several experiments that were conducted it is apparent that fuming nitric acid is capable of mono-nitrating lauric acid. The isolation of the nitro acid itself was not accomplished, but esterification of the mixed reaction products yielded a constant-boiling fraction that was shown to be ethyl nitro-laurate. When attempts were made to distill the unesterified reaction products, decomposition set in, and the resulting high-boiling oil that was obtained was very difficult to purify. The apparent loss of carbon dioxide during the distillation is to be expected of an α -nitro acid, and it seems most probable that the resulting yellow oil was nitroundecane. Although the nitrated material was constant-boiling it contained a non-nitrogenous acid which could be partially removed by repeated washings with hot water. The properties of the acid agree with those of sebacic acid. Complete removal of the acid was not accomplished in spite of exhaustive treatment with hot water and the residual oil gave low nitrogen analyses. Attempts to reduce the material to an amine were unsuccessful. In spite of the conflicting data that has thus far been obtained on the nitrated lauric acid it seems that the most reasonable interpretation of the reaction would include the formation of α -nitrolauric acid and the subsequent decarboxylation of this unstable molecule to nitroundecane. Further experiments will be required to definitely establish this mechanism.

Fuming nitric acid reacted with ethyl laurate to yield lauric acid, oxidation products, and the same high-boiling nitrated oil that was obtained from the nitration of lauric acid. Hydrolysis took place under these conditions and the products recovered included no esterified material.

The reaction of normal alkyl bromides with sodium sulfide to produce symmetrical thio ethers was successfully extended to the formation of high-molecular-weight sulfides. n-Dodecyl, n-tetradecyl, n-hexadecyl, and n-octadecyl bromides reacted with alcoholic sodium sulfide to yield the corresponding thio ethers. These were converted to the sulfoxides and sulfones in very good yields. These reactions demonstrate that the higher-molecular-weight alkyl halides undergo the same reactions as their lower homologs and show that the principle of homology may be extended to these long-chained compounds. The regular variation in the melting points of these series of sulfides, sulfoxides and sulfones is shown in Fig. II (139).

The ease with which the sulfoxides and sulfones are prepared makes these compounds the logical derivatives of the thio ethers.

In view of the success that has been attained with certain long-chained sulfur compounds in the field of insecticides, several of the sulfides, sulfoxides and sulfones prepared in this work are being tested for insecticidal activity. The results of this investigation have not as yet been ascertained. The use of sulfur-containing organic substances and of long-chained compounds such as stearic acid in the processing of rubber suggests the possible use of these thio ethers and their oxidation products in this field.

Less success was had in reactions designed to yield sulfonal-type compounds. n-Dodecyl mercaptan could not be made to react with acetone under conditions that have been successfully used with lower-molecular-weight mercaptans. The use of zinc chloride in the reaction as a more drastic

(139) The greater part of the data used in this figure was taken from a paper by the author (82).

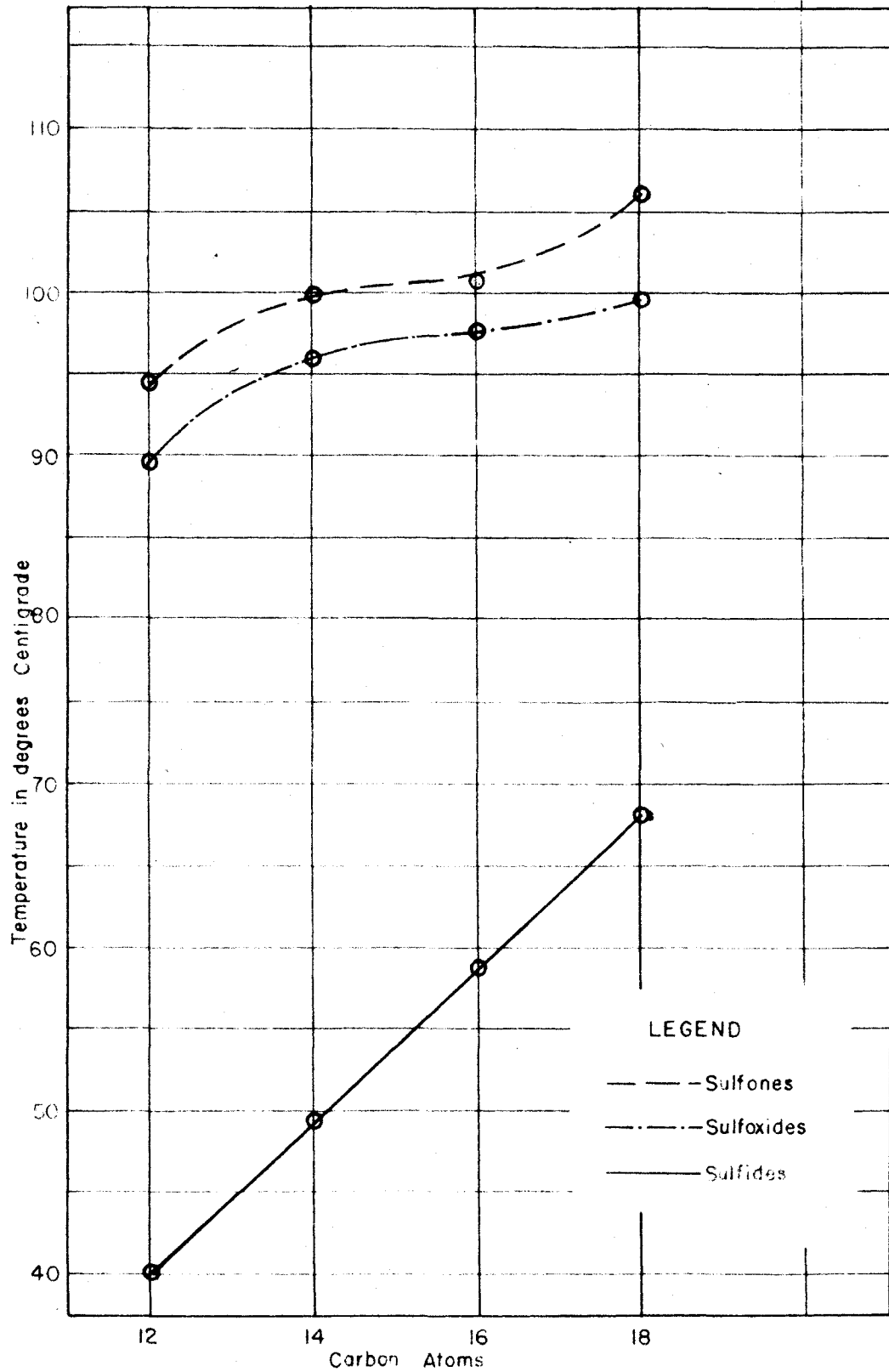


Fig. II. Melting Points of Sulfides, Sulfoxides and Sulfones

dehydrating agent was of no effect and the mercaptan was recovered unchanged. Several modified reactions were designed to yield the desired type of product, but in no case was the anticipated compound formed. 2, 2-Dichloropropane, diethyl dibromomalonate, and diethyl α -bromosuccinate each failed to react with n-dodecyl mercaptan, but such reactions yielded, instead, n-dodecyl disulfide or n-dodecyl sulfide, depending on the conditions used to prepare the metal mercaptide. It was observed that in every case where alcoholic potassium hydroxide was used to form the mercaptide, n-dodecyl disulfide was the product. Inasmuch as the same result could be obtained in the absence of oxygen it was apparent that the active halogen atoms in halogenated compounds acted as the oxidizing agent and converted the mercaptan to the disulfide. The oxidative action of halogenated compounds on mercaptans has been previously observed (140). In cases where sodium metal was used to form the metal mercaptide, the product was always n-dodecyl sulfide. The formation of this product was somewhat surprising and a more critical study of the reaction showed that sodium metal alone is capable of converting the mercaptan to the sulfide. A review of the literature has failed to reveal other examples of this type of reaction. However, Claesson (130) observed that sodium ethyl mercaptide could be prepared by adding sodium metal directly to the mercaptan, or more suitably to an ether solution of the mercaptan. He also observed that the sodium mercaptide could be heated to 200° without decomposition. Above that temperature it decomposed into ethyl sulfide and sodium sulfide. The reaction mixtures in the present experiments were never heated above the

- (140) (a) Nekrosov and Melnikov, Ber., 62 B, 2091 (1929),
(b) Zeigler and Connor, J. Am. Chem. Soc., 92, 2596 (1940).

boiling point of water, but it is conceivable that the long-chained mercaptides are more easily decomposed than sodium ethyl mercaptide. The failure of n-dodecyl mercaptan to react with acetone must be ascribed to the lower reactivity of the mercaptan and would seem to indicate a limitation in the application of the principle of homology to compounds of high-molecular-weight.

The long-chained mercaptans included in this work have appeared previously in the literature, but uncertainties exist regarding the melting point reported for n-octadecyl mercaptan. Collin and co-workers (121) give 56° as the melting point of this substance. The compound described in this thesis melted sharply at 31° and was converted to derivatives whose constants are in complete agreement with those previously reported. The lower melting point for the mercaptan is indicated in the report of Snell and Weisberger (141) who describe n-octadecyl mercaptan as a viscous liquid boiling at 165-170° at 1 mm. In view of the great ease with which the mercaptan may be oxidized to the higher-melting disulfide it seems quite probable that the product obtained by Collin was a mixture of the mercaptan and the disulfide.

Stearonitrile was successfully converted to water-soluble material by means of fuming sulfuric acid. Concentrated sulfuric acid did not sulfonate the nitrile, but this reagent brought about hydrolysis to form stearamide. A mixture of concentrated sulfuric acid in acetic anhydride and chlorosulfonic acid alone were each incapable of introducing sulfonic acid groups into the molecule under the conditions employed. Fuming sulfuric acid, however, converted the nitrile into sulfonated water-soluble material which

(141) Snell and Weisberger, J. Am. Chem. Soc., 61, 459 (1939).

was recovered as the barium salt in 40% yield. The dark water-soluble salt gave indications of the presence of nitrogen and sulfur but was not purified sufficiently to permit significant analysis.

Stearic acid was unattacked by mixtures of fuming sulfuric acid in tetrachloroethane, chlorosulfonic acid in carbon tetrachloride, nor by fuming sulfuric acid alone at room temperature. With fuming sulfuric at 50°, however, a vigorous reaction took place and considerable sulfur dioxide was evolved, indicating that oxidation was taking place. Part of the stearic acid became soluble in water and neutralization of the aqueous solution with barium carbonate yielded a dark brown water-soluble barium salt. The soluble material that was recovered represented 15% of the stearic acid used in the reaction. Purification of the salt was achieved by precipitation of the material in alcohol. Barium analyses indicated the structure of the compound as the barium salt of mono-sulfonated stearic acid.

These results show that the sulfonation of long-chained aliphatic nitriles and fatty acids is possible. Extensive oxidation accompanies the reaction and renders the purification of the extremely soluble sulfonated material difficult.

SUMMARY

The principle of homology has been studied in its relation to high-molecular-weight aliphatic sulfur and nitrogen compounds and has been found to apply in the cases of long-chained amine salts and amides of the normal carboxylic acids, with long-chained pyrrole derivatives, and with long-chained sulfides, sulfoxides and sulfones. Each of these compounds is formed by reactions similar to those used in preparing lower-molecular-weight homologs and have regular variations in physical properties.

The use of long-chained amine salts has been suggested as derivatives for the identification of carboxylic acids. Sulfoxides and sulfones are indicated as the logical derivatives for long-chained thio ethers.

Limitations in the application of the homology concept were found in attempts to prepare long-chained sulfonal-type compounds, and the low reactivity of long-chained mercaptans in the formation of mercaptols was demonstrated.

The proposed preparation of normal long-chained alcohols from the corresponding amines was found to be subject to serious limitations which restrict this reaction as a method of preparing the alcohols.

Liquid phase nitration of lauric acid has been accomplished. However, the nitrated material was obtained in poor yields and the reaction was secondary to the oxidizing action of the nitrating reagents.

Sulfonation of stearonitrile and stearic acid yielded water-soluble material under conditions which indicate that oxidation is an integral phase of the reaction.

A number of techniques have been developed for applying the reactions

of low-molecular weight compounds to the corresponding long-chained types.

Uses have been proposed for many of the new compounds and some of the substances hold the possibility of becoming commercially important.