pounds are notably superior to those of the aliphatic and cycloparaffinic substituted compounds prepared.

The α-substituted tetrahydropyridines can be reduced easily to the corresponding piperidines with tin and hydrochloric acid.

The following new compounds have been prepared and suitable derivatives reported: α-*n*-butyltetrahydropyridine, α-cyclohexyltetrahydropyridine, α-cyclohexylpiperidine, α-(*p*-tolyl)-tetrahydropyridine, α-(*p*-tolyl)-piperidine, α-(*p*-chlorophenyl)-tetrahydropyridine and α-(*p*-chlorophenyl)-piperidine.

AMES, IOWA RECEIVED MARCH 13, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The Preparation and Cracking of High Molecular Weight Nitriles

BY A. W. RALSTON, H. J. HARWOOD AND W. O. POOL

Introduction

The present work was undertaken with the object of producing from high molecular weight fatty acids, straight chain aliphatic compounds containing less than thirteen carbon atoms per molecule. It was thought that a mixture of compounds containing only straight chains might be obtained if a fatty acid derivative which contained no oxygen were subjected to a cracking process similar to that used in the petroleum industry. The present paper is a report of the preparation and cracking of high molecular weight aliphatic nitriles and the partial identification and separation of the resulting compounds.

In undertaking a study of the cracking of high molecular weight nitriles a satisfactory method was essential for preparing such nitriles in considerable quantities from acids. The ordinary method of amide dehydration by means of agents such as phosphorus pentoxide or phosphorus oxychloride was not to be considered because of the expense of the reagents.

The pyrolysis of amides to produce nitriles in varying yields has been reported by several authors.[1] Weidel and Ciamician[2] obtained capronitrile by passing a mixture of ammonia and caproic acid vapor over red hot pumice. Mitchell and Reid[3] noted the formation of small amounts of nitriles incidental to the preparation of amides by passing ammonia through acids at 160–190°. These authors state that no amide was obtained from either palmitic or stearic acid and very little from lauric acid under their conditions.

Since lower amides are partially converted to nitriles upon distillation it seemed probable that stearamide with a high boiling point might be completely converted to nitrile in this manner. Accordingly, stearamide was distilled at atmospheric pressure. The distillate was found to consist of a mixture of stearonitrile and stearic acid together with some unchanged amide. Evidently the water formed by the dehydration of one molecule of amide had served to hydrolyze a second molecule. The ammonium stearate thus formed decomposed at the temperature of the distillation to ammonia and acid. The condition may be expressed by the following equilibria

$$\mathrm{RCOOH} + \mathrm{NH_3} \overset{\mathrm{I}}{\rightleftarrows} \mathrm{RCOONH_4} \overset{\mathrm{II}}{\underset{+\mathrm{H_2O}}{\overset{-\mathrm{H_2O}}{\rightleftarrows}}} \mathrm{RCONH_2} \overset{\mathrm{III}}{\underset{+\mathrm{H_2O}}{\overset{-\mathrm{H_2O}}{\rightleftarrows}}} \mathrm{RCN}$$

In view of the above result, it seemed probable that stearonitrile could be prepared from stearic acid by heating the acid to a sufficiently high temperature in a stream of ammonia. The ammonia would serve to force reaction I to the right and also to sweep out water as it was formed in reactions II and III. This procedure was carried out and was found to produce stearonitrile in excellent yields.

Two methods were used for the cracking of nitriles. The first consisted in passing the nitrile vapors through a glass tube packed with various catalysts maintained at temperatures of 450 to 600°. The second method was to heat the material in a closed vessel to a temperature of approximately 420°. This procedure gave higher yields than the first method and for this

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(1) Wöhler and Liebig, *Ann.*, **3**, 249 (1832); Boehner and Andrews, THIS JOURNAL, **38**, 2503 (1916); Boehner and Ward, *ibid.*, **38**, 2505 (1916); Hurd, Dull and Martin, *ibid.*, **54**, 1974 (1932).

(2) Weidel and Ciamician, *Ber.*, **13**, 84 (1880).

(3) Mitchell and Reid, THIS JOURNAL, **53**, 1879 (1931).

reason was used to produce most of the "cracked fractions" dealt with in this paper. There was no qualitative difference between the products obtained by the two methods.

A study of cracked material boiling from 100 to 275° showed that it consisted of straight chain nitriles and hydrocarbons, both saturated and unsaturated.

In separating the nitriles from the hydrocarbons two general methods were used; the first depended on chemically altering one or the other of the two classes of compounds, the second employed only the difference in physical properties as a basis of separation. It is apparent that the second method, in which both the nitriles and hydrocarbons are separated and recovered in an unchanged condition, is the more desirable of the two. Two obvious ways of separating nitriles from hydrocarbons consist in hydrolyzing the nitriles to alkali soluble acids or in hydrogenating them to acid soluble amines. Separation by hydrolysis has been accomplished satisfactorily, while work on separation by hydrogenation is in progress. Attempts to separate nitriles from hydrocarbons without chemical reactions of the compounds have thus far depended on the differences in solubilities in various solvents and on differences in adsorption of the nitriles and hydrocarbons on silica gel.

Experimental

The Distillation of Stearamide.—Twenty grams of stearamide (m. p. 108–109°) was distilled from an ordinary distilling flask at atmospheric pressure. The temperature of the vapor was 340°. The fumes were alkaline to moist litmus paper. From the distillate, which weighed 17 g., there were isolated 7.5 g. of stearic acid of m. p. 65.5–68°, 6.1 g. of stearonitrile of m. p. 41.5–42.5° and 1.0 g. of stearamide of m. p. 105–106.5°.

The Preparation of Stearonitrile.—The apparatus is shown in Fig. 1. The reaction flask A was constructed from a 500-cc. Claisen flask. The length of the catalyst D was 30 cm. The total length of the catalyst tube was 70 cm. Stearic acid was placed in A and heated to the desired temperature by means of an electric heater. A stream of ammonia was passed through B. The mixture was so heated that the vapor did not rise above point C, about 15 cm. above the level of the liquid. Excess ammonia, together with water vapor and small amounts of acid, passed up through the catalyst which was maintained at a temperature of approximately 400° by means of the furnace E. The fused aluminum oxide catalyst (6 mesh)[4] used served only to convert into nitrile the small amount of acid carried over by the gas stream. Without the catalyst this acid condensed in the cooler portions of the system in the form of the ammonium salt, thereby plugging the tubes. Temperatures were read with thermocouples J and K. The water was condensed in F and collected in G. Exhaust gases were removed through I.

The apparatus was charged with 284 g. of stearic acid (m. p. 68–69°) and heating was started. When the temperature reached about 150° the ammonia was passed in. By means of the heater the temperature was increased to 330° at which point it was maintained during the course of the experiment. Heating was continued for a total of six hours. The ammonia rate was such that an excess was always present. The crude material in flask A weighed 261 g. and contained 2.2% of stearic acid as determined by titration. The receiver G contained 8.5 g. of mixed amide and nitrile which was discarded.

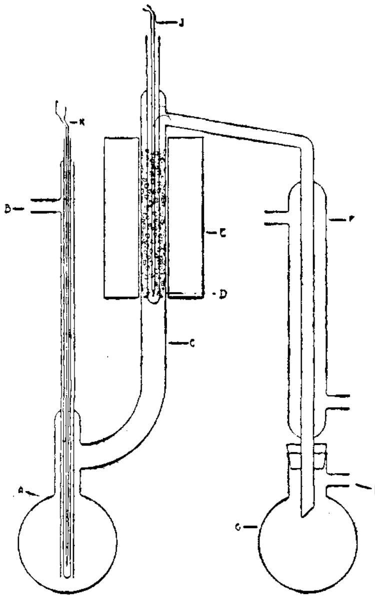

Fig. 1.—Apparatus for preparation of nitriles.

The nitrile was distilled at atmospheric pressure through a 50-cm. Vigreux column. The column was insulated and had an external heater. The nitrile had a boiling range of 352–360°, with about 75% distilling at 356–358°. The distillate weighed 234 g. and contained 3.8% of acid. This corresponds to a yield of 85%. To purify the nitrile further, it was washed with a hot, dilute solution of potassium hydroxide in 50% alcohol, then with hot water until neutral to phenolphthalein. After one crystallization from slightly dilute alcohol, the stearonitrile weighed 206 g., m. p. 41–42°. Pure stearonitrile melts at 42.5–43.0° (corr.).

Vapor Phase Cracking of Nitriles.—The apparatus used was a glass tube (2.5 cm. in diameter) packed with a catalyst and heated by an electric furnace. Temperatures were measured by a thermocouple imbedded in the catalyst. Nitriles of acids obtained from lard were vaporized at a uniform rate and passed over the catalyst in a stream of nitrogen or ammonia gas. The vapors were then con-

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(4) Obtained from the Aluminum Ore Company, East St. Louis, Illinois.

densed and the percentage of material boiling below 275° was determined by distillation. The catalysts used were glass, pumice, aluminum oxide on charcoal, fused aluminum oxide, copper on fused aluminum oxide, and iron on fused aluminum oxide. No evidence was obtained that runs using any one catalyst led to the formation of compounds not present in products obtained when other catalysts were used. Under the same conditions, the yield of cracked material, as measured by the percentage of the total product which boiled below 275°, varied with the nature and age of the catalyst. Fused aluminum oxide gave the highest yield. The uncondensed gases consisted of about half unsaturates, the remainder being saturated hydrocarbons and hydrogen.

Liquid Phase Cracking of Nitriles.—Mixed nitriles, boiling above 275° (1846 g.), made from acids (neutral equivalent of 290.0) obtained from garbage grease were placed in the steel pressure vessel B shown in Fig. 2. The pressure vessel was then heated by a gas flame. When the temperature of the nitriles had reached 330°, as measured by a thermocouple inserted in well C, the valves D and E were closed. After nineteen minutes, the pressure, which was indicated by gage F, was 90 pounds (6 atm.) and the temperature was 415°. Heating was discontinued and the temperature was allowed to drop below 275°. Then the valve E was opened gradually until the pressure had dropped to zero. Heat was applied and all cracked material having a boiling point below 275° was distilled through the water-cooled condenser G. Then valve E was closed and the cycle was repeated. From time to time, additional nitriles were introduced into the pressure vessel through the inlet A until a total of 5538 g. of nitriles had been used. After twenty cracking cycles had been completed, the distillate amounted to 4412 g. (79.7%). The residue in the cracking vessel was a thick, black oil. This residue weighed 550 g. (9.9%). The loss due to uncondensed gases was 576 g. (10.4%) by difference. The distillate was washed with a silver nitrate solution to remove hydrogen cyanide which was always formed. Some of the lower nitriles were removed by this procedure, and the remaining material weighed 4180 g.

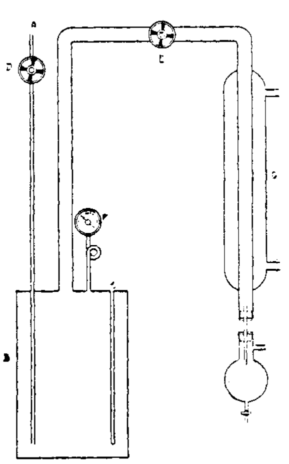

Fig. 2.—Apparatus for cracking nitriles.

Table I

Distillation of Cracked Fraction

Fraction	Weight	Boiling range, °C.	% of total	Nitrogen, %
1	405	30–105	9.7	..
2	609	105–150	14.6	3.54
3	957	150–200	22.9	4.06
4	1019	200–250	24.4	3.65
5	431	250–275	10.3	2.82
Residue	759	>275	18.1	..

The results obtained upon distillation of the 4180 g. of cracked material are shown in Table I.

Identification of Acids Obtained by Hydrolysis of Cracked Fraction.—A sample of miscellaneous cracked fraction (boiling range 100–275°) obtained by the vapor phase cracking of nitriles of acids obtained from lard over various catalysts was hydrolyzed by means of alcoholic potassium hydroxide. The acids obtained were converted into ethyl esters, hydrogenated using platinum catalyst and fractionated.[5] The curve for the second distillation is given in Fig. 3. The S-shaped curves are due to incomplete hydrogenation. The unsaturated esters have higher refractive indices but slightly lower boiling points than the corresponding saturated esters. Hence, an "S" occurs on the distillation curve instead of the usual plateau, due to a slight fractionation of the unsaturated compound from the saturated. Fraction 9 had an iodine number of 5.1.

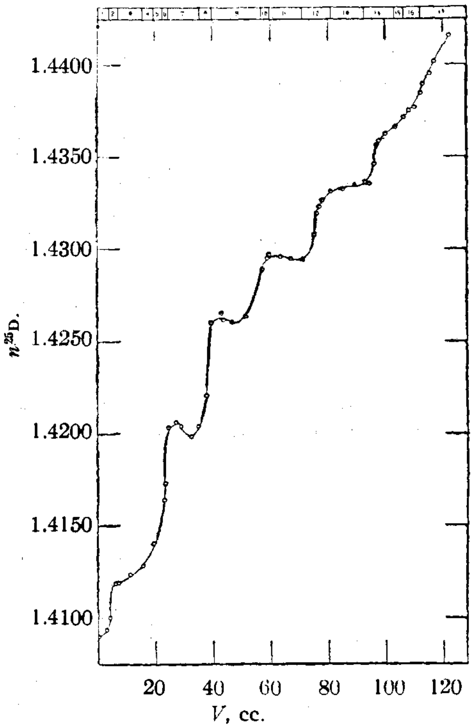

Fig. 3.—Distillation of ethyl esters. Fractions indicated at top.

A 3 to 4 g. sample from each of fractions 1, 3, 7, 9, 11, 13, and 15, Fig. 3, was saponified. The acids obtained were converted into 2-alkylbenzimidazoles according to the procedure of Pool, Harwood and Ralston.[6] The melting points of these derivatives and mixed melting points with derivatives of known acids are given in Table II.

Estimation of the Amounts of Nitriles in Cracked Fractions.—The amounts of nitriles present in several cracked fractions were approximated by hydrolyzing the nitriles and weighing the resulting acids. Fifteen grams of acids

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[5] A 75-cm. column having a 10-mm. inside diameter and a Chromel wire spiral packing was used in all the fractionations in this paper.

[6] Pool, Harwood and Ralston, This Journal, 59, 178 (1937).

TABLE II

MELTING POINTS OF 2-ALKYLBENZIMIDAZOLES

Source of acid	M. p. (corr.), °C.	Mixed m. p., °C.
Fraction 1	153.0–154.0	158–160
Caproic	163.0–163.5	
Fraction 3	135.0–136.0	136.0–136.5
Heptylic	137.5–138.0	
Fraction 7	142.5–143.0	143.0–143.5
Caprylic	144.5–145.0	
Fraction 9	136.5–137.5	138.5–139.0
Pelargonic	139.5–140.5	
Fraction 11	125.5–126.0	125.5–126.0
Capric	127.0–127.5	
Fraction 13	110.5–111.5	110.5–112.5
Undecylic	114.0–114.5	
Fraction 15	104.0–105.0	105.5–106.5
Lauric	107.5	

was obtained from 100 g. of a 30–130° fraction; similarly, 35 g. from a 100–220° fraction; and 37 g. from 100 g. each of 140–160° or 100–275° fraction.

Fractionation of the Hydrocarbons Obtained from Cracked Fraction.—Distillation curves for hydrocarbons obtained from a cracked fraction are given in Figs. 4 and 5. The curve shown in Fig. 4 was obtained by the distillation of a sample of hydrocarbons boiling below 125°. These hydrocarbons were obtained by cracking nitriles of acids obtained from cottonseed oil in a steel vessel under pressure and without a catalyst. The hydrocarbons were purified by washing with water,[7] passing over silica gel, and finally drying with sodium wire. The hydrocarbons were fractionated three times. The fractions were treated with sodium wire after each distillation in order to completely remove traces of nitriles.

The curve shown in Fig. 5 was obtained by the distillation of hydrocarbons from a sample of miscellaneous cracked fractions (boiling range 100–275°). These cracked fractions were prepared by the vapor phase cracking of nitriles of acids obtained from lard over various catalysts. The nitriles were removed from the hydrocarbons by hydrolysis to alkali soluble acids. The hydrocarbons (iodine number 135) were hydrogenated in the vapor phase to an iodine number of 6.8 using a nickel–chromium catalyst. The curve is for the third fractionation. Here, also, the S curves were due to incomplete hydrogenation.

In Table III are given iodine numbers and percentages of unsaturated hydrocarbons for various fractions of the distillation shown in Fig. 4. One double bond per molecule was assumed in calculating these percentages. Qualitative tests for acetylenic linkages were negative.

TABLE III

Fraction	B. p., °C.	Iodine No.	% unsatd. hydrocarbon
1	<37	102.8	28.3% Pentene
4	60–63	154.5	51.1% Hexene
5	63–66	142.3	47.1% Hexene
6	66–69	103.7	34.2% Hexene
7	69–72	89.5	29.6% Hexene
11	93–96	130.3	50.4% Heptene
12	96–99	100.6	38.8% Heptene

Separation of Nitriles from Hydrocarbons by Hydrolysis.—A cracked fraction (2500 g.) having a boiling range of 100–220°, together with 1600 g. of water and 400 g. of sodium hydroxide, was placed in a rocking autoclave and heated to 200°. The time required to attain this temperature was thirty minutes. The heat was then turned off, but the rocking was allowed to continue for an additional ninety minutes during which time the temperature dropped to 100°. The bomb was cooled, the contents were transferred to a separatory funnel, and the lower aqueous layer was drawn off after settling for one hour. The alkaline salt solution was steam distilled for several hours in order to remove a few grams of hydrocarbons which had remained suspended in the aqueous layer. The clear solution was then acidified with concentrated hydrochloric acid, and the resulting upper layer of fatty acids was separated and distilled. The acids weighed 890 g. and had a boiling range of 190° at 760 mm. pressure to 140°

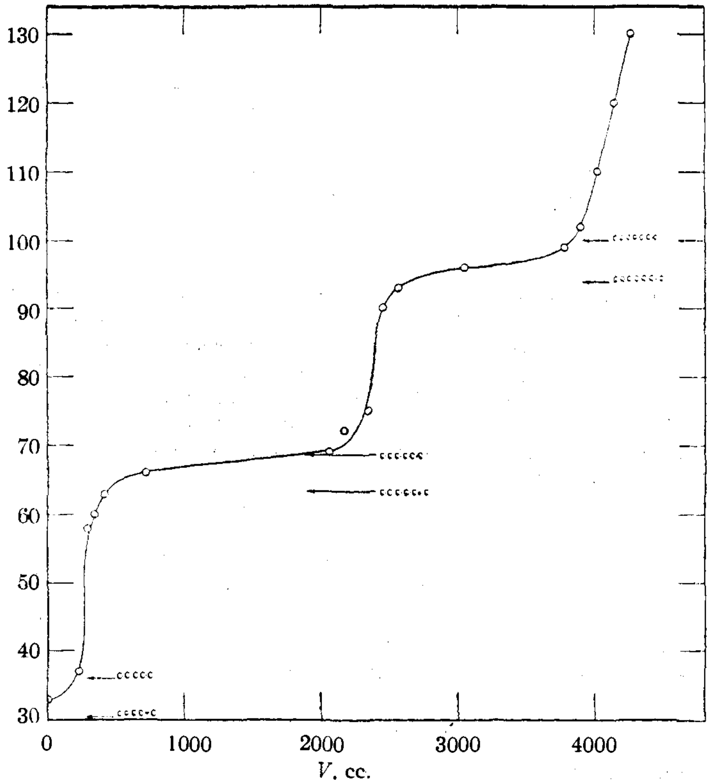

Fig. 4.—Distillation of hydrocarbons. Arrows indicate b. p. of respective compounds.

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(7) Acetonitrile, b. p. 79–81.5°, was isolated from the water washings.

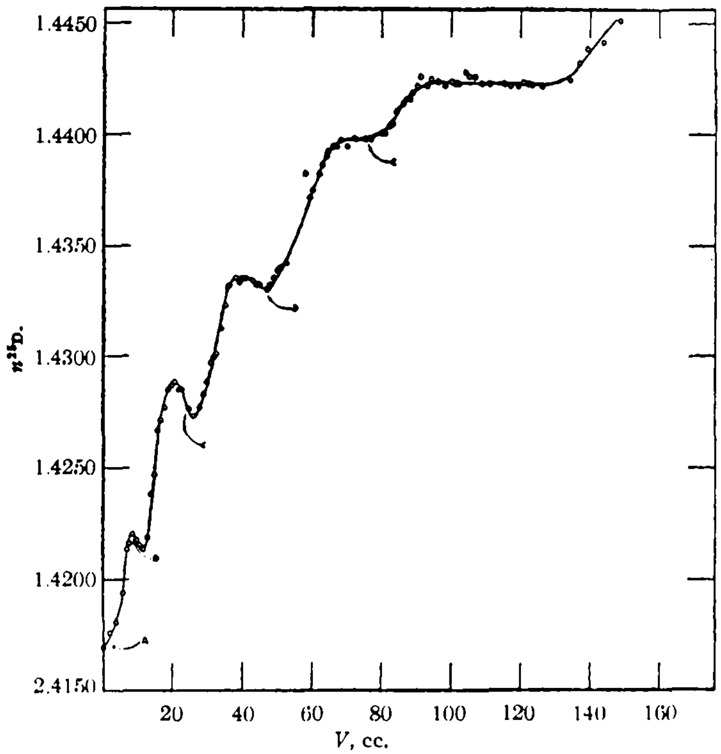

Fig. 5.—Distillation of hydrocarbons: A corresponds to 125° – b. p. of *n*-octane; B to 151° – b. p. of *n*-nonane; C to 174° – b. p. of *n*-decane; D to 195° – b. p. of *n*-undecane; E to 214° – b. p. of *n*-dodecane.

at 5 mm. pressure. The last few drops of the distillate had a molecular weight of 178.

Separation of Nitriles from Hydrocarbons by Solvents.—A sample of cracked fraction having a boiling range of 140–160° was washed three times with concentrated hydrochloric acid, then with water, and finally with dilute potassium hydroxide solution. The cracked fraction was then distilled under vacuum over phosphorus pentoxide. The distillate contained 0.04% fatty acid calculated as caproic and had a nitrogen content of 0.942 g. per 25 cc. The separation of the nitriles from the hydrocarbons by the use of different solvents was studied by the following method: 25 cc. of the cracked fraction was pipetted into a glass-stoppered 50-cc. graduated cylinder. Twenty-five cubic centimeters of the solvent to be tested was added. After thorough shaking, the mixture was allowed to separate into layers at room temperature and the volume of each layer was recorded. An aliquot from each layer was taken with a capillary pipet and the amount of nitrogen was determined. Some typical results are given in Table IV.

TABLE IV

SEPARATION OF NITRILES FROM HYDROCARBONS BY SOLVENTS

Solvent	Upper layer Vol., cc.	Upper layer N. g.	Lower layer Vol., cc.	Lower layer N. g.
100.0% MeOH[a]	13.3	0.049	36.7	0.884
93.8% MeOH[a]	14.8	.088	35.2	.856
93.8% MeOH	9.5	.083	40.5	.860
70.6% MeOH	20.7	.457	29.3	.478
65.2% MeOH[b]	18.0	.239	82.0	.703
70.4% EtOH	19.7	.379	30.3	.563
95.6% Phenol[c]	9.5	.002	42.0	.939

[a] Separation of layers occurred at –77°. [b] Three volumes of solvent were used to one volume of cracked material. [c] Separation occurred at 4°. The volume of the phenol solution used was 26.5 cc.

Adsorption of Nitriles by Silica Gel.—The apparatus used is shown in Fig. 6. Solutions of nitriles were introduced at A and were forced downward through the column of silica gel[8] by nitrogen gas under a pressure of 8 cm. The nitrogen entered the system at B. In some cases the adsorbed material was removed by heat supplied by the electric furnace C. The temperature was ascertained by means of thermocouple D enclosed in a glass tube extending to the bottom of the silica gel. A solution of Eastman valeronitrile in petroleum ether (boiling range 33–50°), containing 24.40 g. of nitrile in a liter of solution, was passed through 16.5 g. of silica gel and the effluent liquid was received in fractions. Results are given in Table V.

A solution of lauronitrile in petroleum ether, containing 16.742 g. of nitrile in a liter of solution, was passed through 18.5 g. of silica gel. Results are given in Table VI.

Separation of the Nitriles from the Hydrocarbons in Cracked Fractions by Adsorption in Silica Gel.—Twenty-five cubic centimeters of cracked fraction similar to that used in the experiments on separation by solvents, was allowed to flow onto a column of silica gel weighing 58 g. The entire 25 cc. was adsorbed or held by capillarity.

TABLE V

ADSORPTION OF VALERONITRILE BY SILICA GEL

Fraction	Vol., cc.	N content, g.	Valeronitrile content, g.	Valeronitrile per 100 cc., g.
Blank	50	0.0003	0.0018	0.003
1	100	.0005	.0030	.003
2	30	.0001	.0006	.002
3	9	.0008	.0048	.053
4	11	.0227	.1346	1.222
5	7	.0290	.1720	2.460

TABLE VI

ADSORPTION OF LAURONITRILE BY SILICA GEL

Fraction	Vol., cc.	N content, g.	Lauronitrile content, g.	Lauronitrile per 100 cc., g.
1	50	0.0004	0.0052	0.010
2	50	.0003	.0039	.008
3	50	.0003	.0039	.008
4	50	.0004	.0052	.010
5	50	.0198	.2560	.512
6	50	.0516	.6672	1.336
7	20	.0242	.3129	1.565

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(8) The silica gel was the "Intermediate Activated" grade of the Silica Gel Corporation, Baltimore, Md.

Forty-five cubic centimeters of petroleum ether (boiling range 33–50°) was allowed to flow over the silica gel in order to wash off the hydrocarbons from the cracked fraction. The effluent liquid was received in a Kjeldahl flask, and the petroleum ether was removed by evaporation on a steam-bath. The hydrocarbons remaining in the flask had an approximate volume of 20 cc. and contained 0.0004 g. of nitrogen. Ammonia gas was then passed over the silica gel, which became warm and the temperature of the column was further increased by heat from the surrounding furnace until a final temperature of 400° had been attained. The heat caused a displacement of 2.0 cc. of water and 6.1 cc. of nitriles. The nitriles were washed thoroughly with hydrochloric acid to remove ammonia preparatory to analysis for nitrogen. The 6.1 cc. contained 0.861 g. of nitrogen.

Discussion

While the pyrolytic decomposition of amides to yield nitriles and water is well known, the simultaneous dehydration and hydration to yield nitriles and acids has not been reported previously. Apparently, in the case of stearamide, the nitrile and acid are formed in equimolecular amounts. Experiments not reported indicate that a similar reaction occurs in the case of lauramide.

The method described here for the preparation of nitriles is distinguished from older methods in that it is carried out in the liquid phase and in the absence of catalysts and produces almost theoretical yields of nitriles. The method has been applied to a variety of higher fatty acids and has been carried out on a very much larger scale in iron vessels.

Sufficient evidence has been presented to indicate the composition of the material produced by the cracking of high molecular weight nitriles. Certain conclusions in regard to the total composition of the cracked material are based on data obtained from restricted fractions. The cracked material consisted of a mixture of nitriles and hydrocarbons. Saturated and unsaturated compounds were present in approximately equal amounts in certain hydrocarbon fractions. That the mixture contained only straight chains is indicated by the occurrence of definite plateaus or breaks in the distillation curves of the hydrocarbons and of esters derived from the nitriles (Figs. 3, 4 and 5). In the volume–refractive index curves (Figs. 3 and 5) the breaks are accentuated by the presence of small amounts of unsaturated compounds. In the case of the hydrocarbons these breaks occur at points corresponding to the boiling points of the straight chain compounds. This would not be the case if branched chains had been present in other than very small amounts. The fractionated esters were further identified by means of derivatives. These derivatives showed the presence of straight chain nitriles containing from six to twelve carbon atoms in the particular fraction of cracked material which was used. Since hydrogen cyanide and acetonitrile were identified, it is reasonable to assume that nitriles and hydrocarbons containing from one to seventeen carbon atoms are produced by the cracking process. There was no indication that any particular chain length was predominant.

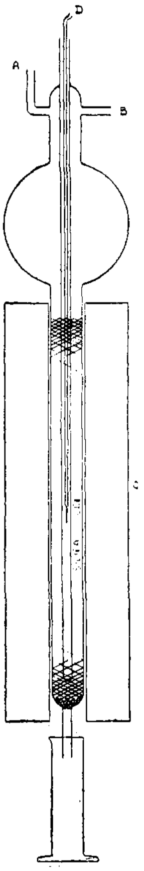


Fig. 6.—Adsorption apparatus.

Because of the similarity in physical properties of nitriles and hydrocarbons, considerable difficulty was experienced in attempting to separate them. Separation by fractional distillation was out of the question as the boiling point of any certain nitrile would have practically coincided with the boiling point of some hydrocarbon of greater chain length. Separation was possible by the preferential solubility of the nitriles in certain solvents from which the nitriles could be recovered unchanged. In Table IV, it is seen that the addition of 25 cc. of 93.8% methyl alcohol to 25 cc. of cracked fraction caused the formation of two layers having volumes of 9.5 cc. and 40.5 cc. Since the smaller layer does not decrease appreciably upon being washed with water, the solvent accounts for 25 cc. of the larger layer. If the solvent were removed by washing with water, 15.5 cc. of cracked fraction containing 0.860 g. of nitrogen would remain. By solvents it is thus possible to separate the cracked fraction into two parts, one of which has a nitrogen percentage 6.3 times as great as that of the other. Such a process would never yield pure nitriles and pure hydrocarbons in one operation, but repeated extractions could be made to give nitriles or hydrocarbons of almost any desired purity. Separation by adsorption appears to be preferable to separation by solvents. From

Table V, fractions 1 and 2 (130 cc.) contained only 0.004 g. of valeronitrile. The original nitrile solution contained 3.172 g. of valeronitrile in 130 cc. Therefore, 16.5 g. of silica gel adsorbed 3.168 g. of nitrile before adsorption ceased to be complete. This amount is equivalent to 19% of the weight of the silica gel. The nitrile can be displaced from the silica gel by means of hot water. By use of the data in Table VI it can be shown that silica gel will adsorb 18% of its weight of lauronitrile from a hydrocarbon solution before small amounts of nitrile appear in the effluent liquid. In the last of the adsorption experiments it is shown possible to remove practically all of the nitriles from a cracked fraction and to recover it after adsorption by heating the silica gel. The original 25 cc. of cracked material contained 0.942 g. of nitrogen, of which 0.861 g. was accounted for in the material removed from the silica gel by heating. Less than 1% of the nitriles was not adsorbed.

Summary

1. The decomposition of high molecular weight amides by heat has been shown to cause a simultaneous hydration and dehydration which leads to the formation of almost equal amounts of acids and nitriles.

2. A non-catalytic method has been developed for preparation of high molecular weight nitriles from fatty acids and ammonia.

3. High molecular weight nitriles have been cracked in the liquid and vapor phases to yield straight chain hydrocarbons and nitriles.

4. Methods have been described which permit the separation of nitriles from hydrocarbons.

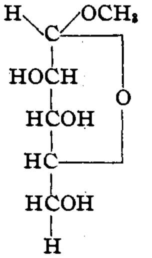
CHICAGO, ILLINOIS RECEIVED NOVEMBER 16, 1936

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Crystalline Alpha-Methyl-*d*-arabinofuranoside[1]

BY EDNA M. MONTGOMERY AND C. S. HUDSON

A new crystalline methyl *d*-arabinoside, which is shown in the accompanying article by Jackson and Hudson to be the alpha form of *d*-arabinofuranoside,[2] has been isolated from the mixture of substances that is obtained by the reaction of *d*-arabinose and methyl alcohol containing hydrochloric acid under mild conditions of glycoside formation. This reaction is accompanied by a double reversal of the sign of optical rotation, as has been reported by previous investigators.[3] The authors were able to crystallize the new furanoside, the rotation[4] of which (+123 in water) is opposite in sign to that of the sugar itself (−105) and to those of its alpha (−17) and beta (−245) methyl pyranosides, by stopping the reaction at its point of highest positive rotation. The substance crystallizes in well formed, clear prisms and the yield is about 9%. Its fast rate of hydrolysis in aqueous acid conforms with the behavior of known furanosides of aldoses. From the present knowledge of the rotation of this alpha form it appears safe to conclude that the rotation of beta-methyl-*d*-arabinofuranoside, a substance now unknown, will be found to be strongly in the levo direction.



Alpha-methyl-*d*-arabinofuranoside, $[\alpha]^{20}_{D}$ +123

Experimental

The removal of solvents and the drying of sirups and crystals were carried out at 25–27° in desiccators supplied with calcium chloride and soda lime and evacuated by a pump. When constant weights were desired the higher vacuum of an oil pump was used for final dryings. The hygroscopic character of the furanoside crystals and the high humidity of the summer atmosphere during the work made it advisable to perform many of the manipulations in dry air. We used a cabinet of 55 × 39 × 43 cm. dimen-

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(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Report of the isolation of this compound was included in a paper entitled "The Oxidation of Alpha and Beta Forms of Methyl *d*-Arabinoside and Methyl *d*-Xyloside," presented by E. L. Jackson and C. S. Hudson at the Pittsburgh meeting of the American Chemical Society, Sept. 7–11, 1936.

(3) Baker and Haworth, *J. Chem. Soc.*, **127**, 365 (1925); Levene, Raymond and Dillon, *J. Biol. Chem.*, **95**, 699 (1932).

(4) Throughout this article the rotations are specific rotations at 20° for sodium light.