

with absolute alcoholic potassium hydroxide and the resulting two isomeric chloroethoxyquinolines were separated and their structures proved.

2. 2,4-Dichloroquinoline, 2-chloro-4-ethoxyquinoline, 4-chloro-2-ethoxyquinoline and 2-chloro-4-hydroxyquinoline were condensed with various amines giving several new amino- and

diaminoquinolines. 4-Chlorocarbostyryl failed to react.

3. 4-Amino-2-ethoxyquinoline failed to react with compounds containing active halogen atoms, however, two derivatives of this amine were prepared.

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RECEIVED JANUARY 20, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Higher Hydrocarbons.¹ I. Seven Alkyl Substituted Docosanes

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While a large amount of excellent work has been done on the systematic study of the lower molecular weight hydrocarbons, there is very little accurate information on hydrocarbons containing over twenty carbon atoms. Outstanding exceptions are the investigations of Mikeska³ and Landa.⁴ Recently another investigation of this type has been reported by Neyman-Pilat and Pilat.⁵ Their work includes the properties of seven C₂₂ hydrocarbons, previously prepared by Turkiewicz.⁶

Approximately two hundred aromatic hydrocarbons in this range have been made by various workers for carcinogenic tests. Unfortunately the study of the other properties has been very limited. For this reason their preparation is of only secondary interest to this work and will not be considered in this paper.

The compounds studied and the methods used in the present work have been carefully selected to avoid complications due to rearrangement or other side reactions. Special emphasis has been placed on the purification of the intermediates. Every effort has been made to obtain a high standard of purity in the finished hydrocarbons.

The purity of the products has been determined by means of time-temperature melting curves. Supplementary evidence has been obtained from distillation-refractive index curves and distillation-viscosity curves. A compound is accepted only if those data indicate a purity of over 95%

(1) American Petroleum Institute Project No. 42; Advisory Committee, L. A. Mikeska, C. R. Wagner and L. C. Beard, Jr., Chairman.

(2) Present address, Reilly Laboratories, Indianapolis, Ind.

(3) Mikeska, *Ind. Eng. Chem.*, **28**, 970 (1936); Mikeska and co-workers, *J. Org. Chem.*, **2**, 499 (1938); **6**, 787 (1941).

(4) Landa and co-workers, *Coll. Czechoslovak. Chem. Commun.*, **4**, 538 (1932); **5**, 204 (1933); **6**, 423 (1934).

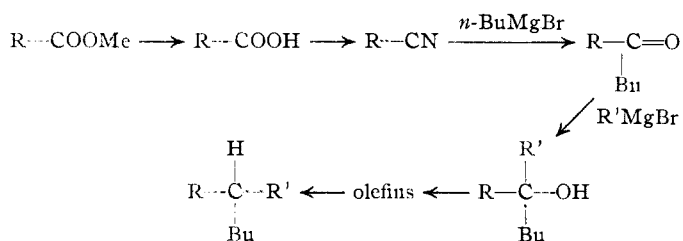
(5) Neyman-Pilat and Pilat, *Ind. Eng. Chem.*, **33**, 1382 (1941).

(6) Turkiewicz, *Ber.*, **73**, 861 (1940).

for a quantity of at least 100 g. Additional checks are given by molecular refraction values and failure to show change in composition on solvent extraction and treatment with silica gel.⁷

In this paper seven simple isoparaffins from C₂₆ to C₃₂ have been prepared and studied. Four of these have a straight C₂₂ chain with *n*-butyl groups on the fifth, seventh, ninth, and eleventh carbon atoms, respectively. The other three have the same C₂₂ chain, but with *n*-hexyl-, *n*-octyl-, and *n*-decyl groups on the seventh, ninth, and eleventh carbon atoms, respectively. By this selection it was possible to vary widely the symmetry of the molecule.

Two general methods of synthesis have been used in the present work. 7-*n*-Butyl-, 9-*n*-butyl-,



and 11-*n*-butyl-docosanes were made in the steps shown. 5-*n*-Butyl-, 7-*n*-hexyl-, 9-*n*-octyl-, and 11-*n*-decyldocosanes were made as follows

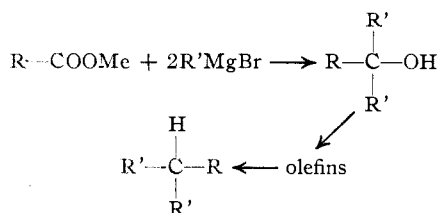


Table I is a summary of the important properties of these hydrocarbons. As the reason for

(7) Mair and White, *J. Research Natl. Bur. Standards*, **15**, 51 (1935); Willingham, *ibid.*, **22**, 321 (1939)

TABLE I
THE PROPERTIES OF THE SEVEN ALKYL SUBSTITUTED DOCOSANES

Docosane	Empirical formula	Melting point, °C.	Boiling point at 1.0 mm., °C.	n_D^{20}	d_4^{20}	Molecular refraction		Viscosity at 20° (centipoises)
						Found	Calcd.	
11- <i>n</i> -Butyl-	C ₂₆ H ₅₄	0.0	194	1.4500	0.8046	122.2	122.3	15.35
9- <i>n</i> -Butyl-	C ₂₆ H ₅₄	1.3	193	1.4498	.8041	122.3	122.3	15.65
7- <i>n</i> -Butyl-	C ₂₆ H ₅₄	3.2	194	1.4499	.8040	122.3	122.3	16.48
5- <i>n</i> -Butyl-	C ₂₆ H ₅₄	20.8	195	1.4503	.8057	122.1	122.3	17.15
7- <i>n</i> -Hexyl-	C ₂₈ H ₅₈	19.3	209	1.4517	.8078	131.5	131.5	18.55
9- <i>n</i> -Octyl-	C ₃₀ H ₆₂	8.6	222	1.4537	.8112	140.8	140.7	22.25
11- <i>n</i> -Decyl-	C ₃₂ H ₆₆	1.0	235	1.4543	.8127	150.0	150.0	25.88

the synthesis of the compounds was to obtain data useful in establishing the chemical composition of lubricating oils, a large number of other properties are being determined. This information will soon be published in the appropriate journals together with the related generalizations.

With the exception of one hydrocarbon, 11-*n*-decyldocosane, those given in this paper have not been reported before. The preparation of that compound by Klos, Neyman-Pilat and Pilat⁸ came to our attention after the completion of our work. The properties of the two preparations agree well.

Experimental

Intermediates.—The greatest of care has been used in obtaining pure intermediates. Fractional distillation columns⁹ with 25–35 theoretical plates have been used in all cases where distillation was possible. Where it was impossible to use these efficient columns a less efficient column or a Claisen flask was used together with repeated recrystallizations. The properties of the intermediates are given in Table II.

The importance of great care in the purification of the intermediates cannot be overemphasized. Unless the starting materials are free of isomers or closely similar impurities it is hopeless to try any purifications of the hydrocarbons prepared from these intermediates. For this reason we give rather complete data on our intermediates.

(a) **Bromides.**—These were prepared from the technically available alcohols. The alcohols were refluxed with the mixture of hydrobromic acid and sulfuric acid formed in the reduction of bromine with sulfur dioxide.¹⁰ The ratios were usually 8 moles of alcohol to 15 moles of hydrobromic acid. Refluxing generally was continued for twenty-four to thirty-six hours. The alkyl bromides were then separated from the acid solutions by steam distillation. The products were washed with half their volumes of cold 95% sulfuric acid, next with ammoniacal methanol-water solution and finally with water. After drying several days over anhydrous potassium carbonate,

the bromides were distilled through an all glass column of 25–30 theoretical plates.

(b) **Methyl Esters.**—The esters of lauric, myristic, and palmitic acids were prepared in large runs by the methanalysis of coconut oil and bayberry wax.¹¹ These crude esters after washing with water and drying over calcium chloride were distilled through columns of 25–35 theoretical plates.

The methyl oleate was prepared by refluxing 1060 g. of oleic acid (Eastman Kodak Co. technical), 1500 cc. of methanol, and 75 cc. of concentrated sulfuric acid for thirty-six hours. After washing and drying, the product was distilled with difficulty through a 25-plate column at 5 mm.

(c) **Acids.**—Lauric, myristic, and palmitic acids were prepared in almost quantitative yields from the saponification of the pure methyl esters.

(d) **Nitriles.**—Following the procedure of Ralston, Harwood and Pool¹² the lauro-, myristo- and palmito-nitriles were prepared in good yields by passing ammonia through the molten acids at 290–300°. The nitriles were then distilled at 10 to 30 mm. through a 25-plate column.

(e) **Butyl Ketones.**—5-Hexadecanone, 5-octadecanone, and 5-eicosanone were prepared by adding lauro-, myristo- and palmito-nitriles, respectively, to a slight excess of *n*-butylmagnesium bromide in runs of 1.5 to 2.0 moles. The Grignard addition products were decomposed with excess dilute sulfuric acid and ice. After separation of the ether layer and extraction of the water layer with 500 cc. of ether, the combined solutions were stripped of ether and the crude ketone distilled through a modified Claisen flask at 1.0 to 3.0 mm. The best fractions were then recrystallized from ethyl acetate.

11-*n*-Butyldocosane¹³.—A Grignard solution was prepared from 212 g. (0.96 mole) of decyl bromide in the usual manner. To this was added 97 g. (0.43 mole) of 5-hexadecanone dissolved in 500 cc. of anhydrous ether. After stirring overnight the mixture was hydrolyzed with ice and a slight excess of sulfuric acid. After separation and ether extraction, the ether was distilled off and the residue was fractionated under vacuum in a modified Claisen flask. The tertiary alcohol was dehydrated at 175–180° on anhydrous copper sulfate in an atmosphere of nitrogen.

The resulting olefins were filtered through a short column of silica gel to remove the copper sulfate and other

(8) Klos, Neyman-Pilat and Pilat, *J. Applied Chem.* (U. S. S. R.), **13**, 1369 (1940).

(9) To be described in a separate publication to be submitted to the *Analytical Edition of Industrial and Engineering Chemistry*.

(10) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. I, 1932, p. 23.

(11) An adaptation of the method of "Organic Syntheses," Vol. XX, p. 67.

(12) Ralston, Harwood and Pool, *THIS JOURNAL*, **59**, 986 (1937).

(13) See Table 1.

TABLE II
 PROPERTIES OF THE INTERMEDIATES

Compounds	Yield, ^a %	n_D^{20}	Melting ^b point, °C.	°C.	Boiling ^c point Mm. press.
Bromides					
<i>n</i> -Butyl bromide	85-90	1.4392		100	740
		1.4392 (W) ^c		99.5	734 (W)
<i>n</i> -Hexyl bromide	75-85	1.4478		155	738
		1.4479 (H)		156	760 (H)
<i>n</i> -Octyl bromide	65-80	1.4527		111	47
				201	760 (H)
<i>n</i> -Decyl bromide	70-75	1.4558		124	20
				118	15 (H)
Methyl Esters					
Methyl laurate	Over-all yields of pure esters	1.4320		140	15
				141	15 (H)
Methyl myristate	75-85% on basis of coco- nut oil or bay- berry wax	1.4369	19	140	5
			18.8 (F)	155-157	7 (H)
Methyl palmitate			29	163	5
			29.2 (F)	184	12 (H)
Methyl oleate	60	1.4530		175	5
				212-213	15 (H)
Fatty Acids					
Lauric acid	95		44, 43.7 (F)		
Myristic acid	93		54, 54.4 (F)		
Palmitic acid	95		63, 62.9 (F)		
Nitriles					
Lauronitrile	75-85		4	160	30
			4 (R)	198	100 (R)
Myristonitrile	75-80		19	168	12
			19 (R)	169	13 (R)
Palmitonitrile	80		31	173	7
			31 (R)	251.5	100 (R)
Butyl Ketones					
5- <i>n</i> -Hexadecanone	68		36-37	145	2
5- <i>n</i> -Octadecanone	70		44-45	170	2
5- <i>n</i> -Eicosanone	60		53-54	195	2

^a The yields are calculated on the basis of the *pure* intermediates. ^b The temperatures are not corrected. ^c Sources of the literature values are indicated: (W) Whitmore, Karnatz, and Popkin, *THIS JOURNAL*, **60**, 2540 (1938); (H) Heilbron "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1936; (F) Francis and Piper, *THIS JOURNAL*, **61**, 577 (1939); (R) Ralston, Harwood, and Pool, *ibid.*, **59**, 986 (1937).

impurities. This purification makes hydrogenation much easier. The almost water-white olefins were then charged into a high pressure bomb.¹⁴ The hydrogenation was more than 95% complete in less than an hour at 1800 lb. per sq. in. and 170° over U. O. P. nickel.¹⁵ Shaking was continued for five hours to ensure complete hydrogenation. The nickel was removed by filtration and the product distilled slowly at 0.5 mm. through the high vacuum column⁹ (an efficiency of 4-5 theoretical plates). The fractions having constant refractive indices were passed through a column of silica gel to yield the water-white, odorless isoparaffin. Table III gives percentage yields and summary of analyses.

9-*n*-Butyldocosane and 7-*n*-Butyldocosane.—These were prepared in the same manner as 11-*n*-butyldocosane. In the synthesis of each of these, runs of approximately 1 mole were made.

5-*n*-Butyldocosane.—A tertiary alcohol was prepared by the addition of 296 g. (2.0 moles) of methyl oleate to the Grignard reagent prepared from 685 g. (5.0 moles) of *n*-butyl bromide. This tertiary alcohol was isolated and dehydrated in the same way as described for carbinol related to 11-*n*-butyldocosane. The resulting diolefins were found to be somewhat easier to hydrogenate and the overall yield was higher.

7-*n*-Hexyldocosane, 9-*n*-Octyldocosane and 11-*n*-Decyldocosane.—The related tertiary alcohols were prepared by the addition of *n*-hexyl-, *n*-octyl-, and *n*-decylmagnesium bromides to the methyl esters of palmitic, myristic, and lauric acids, respectively. The alcohols were dehydrated and the olefins treated as before. In each of these preparations a ratio of 5.0 moles of Grignard reagent to 2.0 moles of ester was used.

Physical Properties.—Every effort has been made to obtain accurate physical properties to the extent justified by the purity of the compounds. The following is a list with

(14) Supplied by American Instrument Company, Silver Spring, Md.

(15) Supplied by the Universal Oil Products Co., Chicago, Ill.

the methods of measurement of those important properties included in this paper.

(a) **Melting Point.**—The melting point of the compound was taken as the "point of break" (solid to liquid) in the time-temperature melting curve.¹⁶ The temperature is reproducible to 0.05° and was measured by a thermocouple standardized by comparison with thermometers checked by the Bureau of Standards. The accuracy of the standardization was 0.1°. The range of melting is not included because it is impossible to determine exactly when the compound begins to melt. A study of the curves indicates that in all cases at least 80% of the substance melted over a range of 1.5° or less.

TABLE III

THE YIELDS, PURITY AND ANALYSES OF THE HYDROCARBONS

Name, docosane	Moles ^a in run	Yield, ^a %	Purity, ^b mole %	Analyses, ^c %			
				Found		Calcd.	
				C	H	C	H
11- <i>n</i> -Butyl-	0.43	73	95-7	84.9	14.4	85.1	14.9
9- <i>n</i> -Butyl-	1.65	75	95-7	85.1	15.0	85.1	14.9
7- <i>n</i> -Butyl-	2.28	79	95-7	85.3	14.4	85.1	14.9
5- <i>n</i> -Butyl-	2.0	85	97	84.6	14.4	85.1	14.9
7- <i>n</i> -Hexyl-	2.0	78	97	84.9	14.6	85.2	14.8
9- <i>n</i> -Octyl-	2.0	80	95-6	85.6	14.4	85.2	14.8
11- <i>n</i> -Decyl-	0.95	75	95-6	85.1	14.5	85.2	14.7

^a Yields and moles in runs are based on the amount of butyl ketone, or of ester used. The percentage given is the yield of pure isoparaffin. ^b The purity of the compounds was calculated from time-temperature melting curves (Ref. 16). With five of these seven compounds difficulties in the interpretation of the data made it impossible to obtain exact values. ^c Approximately twenty of these hydrocarbons now prepared by A.P.I. Project 42 were sent to a commercial analytical laboratory. The values reported by the laboratory indicated that there must be some difficulty in the method of combustion or that our compounds were less pure than we had good reason to believe. To check these results the Esso Laboratories through the courtesy of Dr. L. A. Mikeska ran analyses on several of our compounds. Their checks with the calculated values were very good. The above analysis of the 9-*n*-butyl-docosane is a sample of their results.

(b) **Boiling Point.**—The boiling point was taken from a vapor pressure curve for each compound determined over the range of 0.3 to 5.0 mm. These measurements were made in a special apparatus¹⁷ that was standardized using di-*n*-butyl phthalate before and after. The vapor pressure measurements were determined with a precision of 0.5°. There was no detectable boiling range with the compounds known to be pure (95% or better).

(c) **Index of Refraction.**—The refractive indices were measured at 20.0 = 0.01° using a Valentine "Universal" Abbe type refractometer. The instrument was checked against a series of pure hydrocarbons obtained from the Bureau of Standards. The results are correct to 0.0001 unit.

(d) **Density.**—The densities were measured at 20.0 = 0.01° using pycnometers holding about 5 ml. The values are correct to 0.0002 g. per ml.

(16) A paper giving complete details of this method has been submitted to the *Analytical Edition of Industrial and Engineering Chemistry*.

(17) Fenske, Chapter on "Laboratory and Small-Scale Distillation," *The Science of Petroleum*, Oxford University Press, London, 1938, Vol. II, p. 1634.

(e) **Molecular Refraction.**—The experimental values were obtained by use of the Lorenz and Lorentz equation.¹⁸ The calculated values are based on the Auwers and Eisenlohr atomic values.¹⁸

(f) **Specific Dispersion.**—The values obtained from the drum readings of the refractometer by the use of tables to give values for $(n_D - n_C)/d$ at 20° were about 91-93. It is generally recognized that values for the property obtained in this manner are not entirely reliable. Measurements by different observers will vary by as much as 4%. However, this order of accuracy is of value as there are much greater differences between isoparaffin and aromatic or olefinic compounds. Plans are under way for more accurate measurements by the Bureau of Standards using selected wave lengths of monochromatic light.

(g) **Viscosity.**—The viscosity was measured at 20.0° by the use of a modified Ostwald viscosimeter.¹⁹ The instruments were calibrated against standard oils. These in turn are based on water as having a viscosity of 1.007 centistokes at 20.0°. The values have an accuracy of 0.02 centipoise.

Purity of the Hydrocarbons

Throughout this paper inferences have been made relating to the methods of obtaining pure high molecular weight hydrocarbons. As this is the first of a series of papers it seems necessary to discuss the general problem of purity and the influences of impurities on the various properties.

To obtain pure hydrocarbons the intermediates must be of the highest purity and side reactions must not give rise to isomers or other difficultly separable products. This is necessary because of the limitations of purification methods that may be used in the high molecular weight range. The general methods that may be used are distillation, crystallization, adsorption, and solvent extraction.

Distillation of substances boiling in the range of 180-210° (1.0 mm.) is impossible in the conventional packed columns because of the very high pressure drop. Therefore complete separation by distillation through a column⁹ such as has been used in this work cannot be obtained unless there are differences in the boiling point of about 30°. However, the presence of impurities may be detected if they differ by as much as 3° in boiling point.

Crystallization²⁰ has possibilities which may avoid the difficulty found with distillation.

Adsorption on silica gel⁷ has been used throughout this work and is of greatest value if its limitations are understood. Separation occurs only when there are differences in polarity. Moreover, the adsorptive capacity of the gel is limited. Isomeric or homologous mixtures are not changed by its use.

As yet, general use has not been made of solvent extraction. The results are similar to those obtained with silica gel. The method shows much promise and is being developed. Extraction studies²¹ on hydrocarbons not included in this paper showed very definite separation of

(18) Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938, Vol. II, p. 1738.

(19) Cannon and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

(20) Private communication from Dr. F. D. Rossini at the National Bureau of Standards.

(21) By Dr. K. A. Varteressian of this Laboratory.

impurities. However, systematic extractions equivalent to ten stages, using acetone as solvent, on a sample of the 7-*n*-hexyldocosane reported herein gave no indication of any separation.

In spite of the limitations involved in obtaining pure high molecular weight hydrocarbons, the problem has been solved to the extent of making compounds of better than 95 mole per cent. purity.

First, all intermediates were prepared in a high state of purity (98.5 to 99.5 mole per cent.). This eliminates all but a maximum of 3.0 mole per cent. of isomeric and homologous impurities in the finished product traceable to impure starting material. Second, the reactions used in the synthesis of the hydrocarbons were chosen to minimize the possible side reactions. Isolation of the olefins, intermediate in the syntheses involved a crude distillation, in which impurities differing in boiling point by 50° or more were eliminated. The more polar substances were then at least partly removed by passage of the olefins through silica gel.

The olefins obtained at this stage of the preparation were hydrogenated and the isoparaffins purified. Complete hydrogenation was rather difficult and in many cases as much as 2 per cent. of unchanged olefin remained. The nickel and part of the olefinic and polar impurities were removed by passage through a tube of silica gel. This step was followed by very careful fractional distillation to eliminate all of the impurities boiling as much as 30° from the hydrocarbon. This step also indicates the presence or absence of impurities differing by as much as 3° in boiling point. As a final step and to remove any impurities arising from decomposition in distillation the constant refractive index fractions were passed through silica gel again to give the finished product.

To determine the purity of this finished product is a problem often as difficult as the preparation of the compound. The only exact method is the use of time-temperature cooling or melting curves. With the compounds studied only the melting curve has any value. This is because of the difficulty introduced by the unusual degree of supercooling characteristic of these substances. A method similar to that described by Mair, Glasgow and Rossini²² was used. Certain modifications¹⁶ were necessary due to the properties of our compounds. The method is useless when glasses are formed and may not give exact values in many cases if stereoisomers are present, or if there is a change in crystalline form in the process of melting.

As a check on the purity of the hydrocarbons, carbon and hydrogen analyses such as the ones reported in this paper are valueless. For this purpose it would be necessary to have an accuracy²³ approaching atomic weight

(22) Mair, Glasgow and Rossini, *J. Res. Natl. Bur. Standards*, **26**, 591 (1941).

(23) Rossini, *Proc. Am. Petroleum Institute*, **18** (111), 44 (1937).

measurements. However, the analyses do serve to indicate that the compounds are hydrocarbons and not oxygenated substances.

There are additional checks on purities that may be of value. These are, in order of importance, the distillation curves, changes on passage through silica gel, the effect of solvent extraction, and properties such as molecular refraction.

If one assumes that impurities are present to the extent of 5.0 mole per cent., the question arises as to what they may be and how they will influence the properties determined. The present methods of purification will not eliminate isomeric impurities. They will eliminate homologous impurities only if there is a difference of at least three carbon atoms. The finished product may pick up traces of moisture and low boiling solvents from the air. To avoid contamination from the bottles used it is necessary to bake out the latter thoroughly. In terms of weight these are insignificant, but in mole per cent. they may be very important. Thus 0.05% by weight of water becomes 1.0 mole per cent.

The presence of 5 per cent. of isomeric impurities would influence only the melting point to any extent. This may be illustrated by comparing the properties of the compounds in Table I. For example the presence of 5 mole per cent. of No. 4 in No. 1 would alter the boiling point of the latter at 1 mm. by about 0.05°, the refractive index by 0.00002, the density by 0.00006 g./ml., the specific dispersion by an insignificant amount, and the viscosity at 20° by about 0.09 centipoise.

Acknowledgment.—We thank our colleagues for their help: N. C. Cook carried out the high pressure hydrogenations; G. H. Fleming and W. S. Sloatman determined the purity of the compounds and their melting points; C. S. Rowland made the measurements on density and viscosity, and R. D. Hinkel did the boiling point determinations.

Summary

1. The preparation and five important properties are given for seven alkyl substituted docosanes.
2. Data on the yields and properties of seventeen intermediates are given.
3. The problem of the purity of such materials is discussed.

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RECEIVED DECEMBER 15, 1941