

2. 7-Methoxy-2-hydroxynaphthaldehyde is converted by a Perkin synthesis to 2-methyl-9-methoxy-4,3- β -naphthopyrone. This compound brominates or nitrates in the 10-position. The resulting bromopyrone is hydrolyzed and methylated to β -(2,7-dimethoxy-8-bromonaphthyl)- α -methylacrylic acid. The unbrominated pyrone is also hydrolyzed and methylated and yields β -(2,7-dimethoxynaphthyl)- α -methylacrylic acid. Upon bromination of this acid, the halogen enters the 10-position, simultaneous hydrolysis of the methoxyl group occurs and pyrone formation re-

sults. The mode of preparation of the acrylic acid and the bromoacrylic acid leads to the conclusion that the carboxyl is *cis* to the 2-methoxyl group of the naphthalene nucleus.

3. These acids are both less soluble than the corresponding geometric isomers made directly by the appropriate Perkin reaction on 2,7-dimethoxynaphthaldehyde and bromination. No tendency to pyrone formation appears in this last reaction. The less-soluble acrylic acid is converted to the more soluble by irradiation with ultraviolet light.

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

Higher Hydrocarbons.¹ II. Five 11-Substituted Heneicosanes

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In the first paper² of this series the methods of preparation and the properties for seven alkyl substituted docosanes were given. A brief survey was made of the literature relating to the preparation of hydrocarbons containing more than twenty carbon atoms.

Whereas the first paper covered only isoparaffins, this paper reports on a variety of mixed type compounds. In this group of compounds the paraffin chain remains constant, but different type substituents are located in the 11-position. Changes of this type have considerably greater influence on the properties than moving a side chain or varying the molecular weight.²

Lubricating oil fractions in a given molecular weight range show large variations in properties. From the extensive studies³ of Research Project No. 6 of the American Petroleum Institute these differences in the properties of the various lubricant fractions can only be due to differences in the hydrocarbon type. Therefore, this and future papers will describe series of hydrocarbons in which there are variations in hydrocarbon type. Generalizations on the properties and comparison with those in the literature will be published later.

Special emphasis has been placed on obtaining pure compounds. The requirements of purity and the methods of obtaining and determining the purity have been discussed in the earlier paper.²

The synthesis of these compounds involved the addition of an excess of *n*-decylmagnesium bromide to the following esters: ethyl caproate, methyl 2-ethylbutyrate, ethyl cyclopentanecarboxylate, and methyl benzoate. The resulting tertiary carbinols were dehydrated over copper sulfate in an atmosphere of nitrogen. The purified olefins were hydrogenated in a high pressure bomb over various nickel catalysts.

Only one intermediate, ethyl cyclopentanecarboxylate, presented any serious problem. Methods for its preparation in the literature did not seem promising. The method used in this work was the little used reaction⁴ involving the addition of cyclopentylmagnesium bromide to an excess of ethyl carbonate.

With 11-phenyl-11-heneicosanol only one olefin can be obtained on dehydration. Therefore this was isolated and purified as usual. However it is probably an inseparable mixture of the *cis*- and *trans*-isomers.

The selective hydrogenation of the olefinic double bond in the presence of the phenyl group as in the case of 11-phenylheneicosane required special study. It was found possible to carry out this hydrogenation if the olefin was first very carefully purified by distillation and passage through silica gel. The hydrogenation was then carried out at room temperature over very active Raney nickel at a pressure of 1500 to 1800 lb. per sq. in.

Table I is a summary of the important properties of these hydrocarbons. The methods used

(1) American Petroleum Institute Research Project No. 42.

(2) Whitmore, Sutherland and Cosby. *THIS JOURNAL*, **64**, 1360 (1942).

(3) Mair, Willingham and Streiff, *Ind. Eng. Chem.*, **30**, 1256 (1938).

(4) Loder and Whitmore, *THIS JOURNAL*, **57**, 2727 (1935).

TABLE I
THE PROPERTIES OF THE SUBSTITUTED HENEICOSANES AND OF 11-PHENYL-10-HENEICOSENE

$$\begin{array}{c} \text{H} \\ | \\ (\text{C}_{10}\text{H}_{21})-\text{C}-(\text{C}_{10}\text{H}_{21}) \text{ and } (\text{C}_{10}\text{H}_{20})=\text{C}-(\text{C}_{10}\text{H}_{21}) \\ | \\ \text{R} \end{array}$$

R	Formula	M _c , P _c , °C.	B _c , P _c , (1.0 mm.)	n _D ²⁰	d ₄ ²⁰	Molecular refraction		Viscosity 20°C. (centip.)	Moles ^a in run	Yield, ^b %	Purity, ^c mole %	Analyses, ^d %			
						Found	Calcd.					Calcd. C	H	Found C	H
<i>n</i> -Amyl	C ₂₄ H ₅₄	-9.1	192	1.4497	0.8038	122.3	122.3	14.89	1.07	60	95.5	85.1	14.9	84.5	14.7
(3-Pentyl)-	C ₂₈ H ₅₄	forms glass	187	1.4517	.8092	121.9	122.3	15.58	2.25	36	95-7	85.1	14.9	85.5	14.9
Cyclopentyl-	C ₂₄ H ₄₂	-12.7	186	1.4610	.8329	120.1	120.0	20.28	1.89	42	97.1	85.6	14.4	85.7	14.4
Phenyl-10-	C ₂₇ H ₄₆	forms glass	203	1.4922	.8636	124.4	122.8	20.80	3.0	75	97-8	87.7	12.3	87.5	12.0
Phenyl-	C ₂₇ H ₄₈	20.8	204	1.4788	.8531	123.6	123.3	26.41	1.5	95	97.6	87.0	13.0	86.7	12.5
Cyclohexyl-	C ₂₇ H ₅₄	-7.2	209	1.4639	.8373	124.5	124.7	30.23	1.2	95	96.1	85.6	14.0	85.4	14.7

^a In the first four cases based on the ester, in the last two on olefin used. ^b Based on pure hydrocarbon obtained. ^c The purity of the compounds was calculated from time-temperature melting curves. With compounds 2 and 4 glasses were formed on cooling which made the use of melting curves impossible. ^d Analyses of three of the compounds were carried out by the Esso Laboratories through the courtesy of Dr. L. A. Mikeska.

in the measurements and the designations are the same as those given for the earlier series of hydrocarbons.² None of these compounds has been reported before.

Experimental

Intermediates.—The greatest of care has been taken to obtain pure intermediates. Fractional distillation columns⁵ with efficiencies of 25 to 35 theoretical plates have been used on all preparations. The thermometer readings on the boiling points of the intermediates are uncorrected. The constants given are those of the constant boiling point, constant index refraction fractions. Only this material was used as intermediates.

(a) **Decyl Bromide.**—Technical *n*-decanol was refluxed with the hydrobromic and sulfuric acids mixture resulting from the reduction of bromine with sulfur dioxide. This was described in detail in an earlier paper,^{2,6} b. p. 124° (20 mm.); *n*_D²⁰ 1.4558; yield 73%.

(b) **Cyclopentyl Bromide.**—This was prepared by passing hydrogen bromide into pure cyclopentanol at 100°. This was washed with one-half its volume of cold 95% sulfuric acid and then twice with an equal volume of water. After drying for twenty hours over anhydrous potassium carbonate, the product was distilled through an all-glass 25-plate column. The yield of pure bromide was 70%; b. p. 137° (737 mm.); *n*_D²⁰ 1.4890.

(c) **Ethyl Caproate.**—Eastman Kodak Co. technical ethyl caproate was carefully fractionated: b. p. 165° (730 mm.); *n*_D²⁰ 1.4078.

(d) **Methyl 2-Ethylbutyrate.**—Technical 2-ethylbutyric acid obtained from Carbide and Carbon Chemicals Corp. was dried over calcium chloride for several days. Of this, 812 g. (7.0 moles) was added to 2.0 l. of anhydrous methanol and 100 cc. of concentrated sulfuric acid. A heavy precipitate of calcium sulfate formed. This was filtered off, and the clear solution refluxed for four days. Part of the excess methanol was distilled off, and the reac-

tion mixture then diluted with twice its volume of water. The ester layer was separated, and the water layer extracted with ether. This after drying over anhydrous sodium sulfate was fractionally distilled. The yield of pure ester was 75%, b. p. 134° (728 mm.); *n*_D²⁰ 1.4018.

(e) **Ethyl Cyclopentanecarboxylate.**—Cyclopentylmagnesium bromide was prepared from 62 g. (2.5 moles) of magnesium, 363 g. (2.4 moles) of cyclopentyl bromide, and 500 cc. of anhydrous ether. After standing overnight the Grignard solution was removed from the reaction flask under an atmosphere of nitrogen, and filtered. The Grignard solution was added to 590 g. of distilled diethyl carbonate in 500 cc. of anhydrous ether over a period of five hours, with stirring, while the mixture was cooled in an ice-bath. After standing overnight the mixture was decomposed by pouring over crushed ice containing 35 cc. of concentrated sulfuric acid. Two such runs were made, and the combined products distilled through a 25-plate column; yield 275 g., 48.5%; b. p. 171.9° (737 mm.), 89.3° (45 mm.) (both Cottrell); *d*₄²⁰ 0.9523; *n*_D²⁰ 1.4360. Faworski and Boshowski⁷ report a boiling point of 172-174° (752 mm.).

(f) **Methyl Benzoate.**—Methyl benzoate prepared by students in a preparation course was carefully fractionated; b. p. 95° (25 mm.); *n*_D²⁰ 1.5170.

11-*n*-Amylheneicosane.—A Grignard solution was prepared from 660 g. (3.0 moles) of *n*-decyl bromide and 73 g. (3.0 moles) of magnesium in the usual manner. Titration of a sample of the Grignard solution indicated a yield of 95%. To this was added 154 g. (1.07 moles) of ethyl caproate. After stirring for several hours and allowing to stand overnight, the reaction products were poured on 1700 g. of ice and 150 cc. of concentrated sulfuric acid. After standing overnight the ether layer was separated and the water layer was extracted with ether. These ether solutions were combined and the ether removed by distillation through an indented column. In this preparation the tertiary alcohol was isolated. Distillation of the crude products indicated 80 g. of decane, 40 g. of 7-hexadecanone, and 345 g. of di-*n*-decylamylcarbinol; b. p. 225-229° (1 mm.); *n*_D²⁰ 1.4580).

The tertiary alcohol was then dehydrated over anhy-

(5) Described in a separate publication to be submitted to the *Analytical Edition of Industrial and Engineering Chemistry*.

(6) Recently we have found that these higher alkyl bromides may be prepared in much better yields with less trouble by passing hydrogen bromide from the direct combustion of bromine and hydrogen into the alcohol at 110°.

(7) Faworski and Boshowski, *J. Russ. Phys.-Chem. Soc.*, **50**, 587 (1920).

drous copper sulfate in an atmosphere of nitrogen at 160–180°. The olefins were passed through a 50 × 1.5 cm. tube of silica gel. This step gave a water-white product, 310 g., which was then hydrogenated over 20 g. of U. O. P. nickel catalyst⁸ at 120° and 1100 lb. per sq. in. pressure. At least 95% of the required hydrogen was absorbed in ten minutes. Hydrogenation conditions were continued for three hours to ensure completion. The nickel was removed by filtration and the product distilled slowly through the high vacuum column.⁵ The fractions having constant refractive indices were combined and passed through a column of silica gel. The product, 11-*n*-amylheneicosane, was water-white and odorless. Table I gives the percentage yields and the analyses.

11-(3-Pentyl)-heneicosane and 11-Cyclopentylheneicosane.—These were prepared from the appropriate esters in the same manner as the 11-*n*-amylheneicosane. In each case approximately 2 moles of the ester was used. The tertiary alcohol was not isolated.

11-Phenyl-10-heneicosene.—In the usual manner a 7-mole Grignard solution was prepared from pure *n*-decyl bromide. To this was added 408 g. (3.0 moles) of methyl benzoate dissolved in an equal volume of ether. After stirring for a total of ten hours and allowing to stand overnight, the product was poured on ice and 200 cc. of concentrated sulfuric acid. The ether-product layer was separated and the water layer extracted once with 800 cc. of ether. These were combined, the ether removed, and most of the low boiling by-products (*n*-decane), etc., removed by distillation from a modified Claisen flask at 20 mm. pressure. The crude tertiary alcohol was then dehydrated over anhydrous copper sulfate at 160° in an atmosphere of nitrogen. This was then filtered through a column of silica gel to give an almost water-white product. Following this step the crude olefin was distilled through the vacuum column at a pressure of 0.95 mm. Ninety per cent. of the distillate had a constant index of refraction. These constant fractions were combined and passed through silica gel again to give a water-white, odorless finished product.

11-Phenylheneicosane.—The obtaining of this compound by the selective hydrogenation of the related olefin,

11-phenyl-10-heneicosene, required special study. The first two attempts failed. In the first, complete hydrogenation of the olefinic double bond was not obtained and in the second, hydrogenation of the phenyl group took place to the extent of about 5%. This was shown by the melting point curves, systematic solvent extraction⁹ using acetone as a solvent, and chemical test.

It was found that if the olefin was purified (see the preparation of 11-phenyl-10-heneicosene) to the greatest possible extent, hydrogenation of 560 g., 1.5 moles, of the olefin proceeded smoothly and completely in a period of six hours over 30 g. of very active Raney nickel at room temperature and 1800 lb./sq. in. pressure of hydrogen. The product was then filtered through silica gel to remove the nickel and any remaining olefin. Distillation of the product through the vacuum column gave no evidence of other substances being present. All fractions had exactly the same index of refraction. This was not found in the other two attempts to prepare the compound. Some indication of separation was found if the compound was under or over hydrogenated.

11-Cyclohexylheneicosane.—The combined fractions, 445 g., 1.2 moles, from the distillations of the attempted preparations of 11-phenylheneicosane were combined and completely hydrogenated over 25 g. of U. O. P.⁸ nickel at 150° and 1500 to 1800 lb./sq. in. pressure of hydrogen in a time of ten hours. The product was filtered through a tube of silica gel to remove the nickel and any remaining aromatic compounds. This product was then distilled through the vacuum column at 0.5 mm. Ninety-five per cent. of the distillate had a constant index of refraction. These constant fractions were combined and passed through a tube of silica gel a second time. This gave a water-white, odorless product.

Summary

The methods of preparation and six important properties of six new high molecular weight hydrocarbons are given.

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

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