treated with 10 ml. of an alcoholic solution of potassium hydroxide in the cold; allow about half the acetone to evaporate, and add 20 ml. of water to dissolve the potassium bromide and precipitate the red tetraphenyleneethylene; crystallize from hot carbon tetrachloride; m. p. 185–187°; yield 62%.

Factors Affecting the Rate of Bromination.—The photochemical bromination of fluorene shows the marked negative catalytic effect of sulfur, which has been found to characterize side-chain brominations.[3] A solution of 1.66 g. of fluorene and an equivalent amount of bromine in 30 ml. of carbon bisulfide in a glass-stoppered flask was discolorized within thirteen seconds under the mercury arc. A similar solution to which 0.1 g. of sulfur had been added was exposed for 195 seconds; titration showed that only 35% of the bromination had taken place.

The photochemical bromination of fluorene does not show the pronounced negative catalytic effect of moisture, which has been observed in the bromination of ketones.[4] When the experiments in the preceding paragraph were repeated, after adding 1.0 ml. of water to each, the results in both were the same as without the water.

Summary

1. 9-Bromofluorene may be prepared in 60–64% yields by the photochemical bromination of fluorene.
2. 9-Bromofluorene is readily hydrolyzed in hot aqueous solution.
3. The photochemical bromination shows the pronounced negative catalytic effect of sulfur, which characterizes side-chain brominations.

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[3] J. R. Sampey, F. S. Fawcett and B. A. Morehead, THIS JOURNAL, **62**, 1839 (1940).

[4] J. R. Sampey and E. M. Hicks, *ibid.*, **63**, 1098 (1941).

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

Higher Hydrocarbons.[1] IV.[2] Six Phenyleicosanes and Six Cyclohexyleicosanes

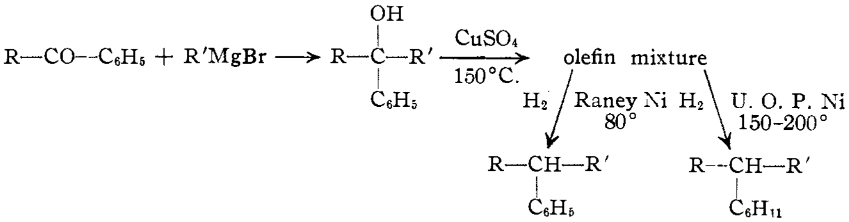
BY FRANK C. WHITMORE, ROBERT W. SCHIESSLER, C. S. ROWLAND[3] AND J. N. COSBY[4]

In the continuation of our work on the synthesis and properties of high molecular weight hydrocarbons, the preparations of twelve new monocyclic hydrocarbons are now reported. As pointed out in the second paper[2] of this series, the large variations in physical properties of lubricating oil fractions in a given range of molecular weight is probably primarily due to differences in molecular type; nevertheless, it is important to have a knowledge of the property variations which may be attributed to positional isomers. The present work is aimed at clarifying the latter problem, at least as regards monocyclic derivatives of the paraffins.

Each of the hydrocarbons reported herein consists of a normal twenty-carbon paraffinic chain, with a phenyl or cyclohexyl group attached to one of the chain carbon atoms. They are the 2-, 3-, 4-, 5-, 7- and 9-phenyleicosanes, and the 2-, 3-, 4-, 5-, 7- and 9-cyclohexyleicosanes. The isomers containing the phenyl and cyclohexyl groups in the 1-position, 1-phenyleicosane and 1-cyclohexyleicosane, were reported in the third paper[2] of the series.

The phenyleicosanes were synthesized by adding the appropriate phenone to excess of the appropriate alkylmagnesium bromide. For example, the preparation of 7-phenyleicosane involved the addition of myristophenone to excess *n*-hexylmagnesium bromide. The resulting tertiary carbinols were dehydrated by heating with copper sulfate, and the purified olefins selectively hydrogenated over Raney nickel to the final hydrocarbon (Figs. 1 and 2).

GENERAL METHOD OF SYNTHESIS



when $R = CH_3, C_3, C_{11}, C_{13}, C_{15}, C_{17}$
$R' = C_{18}, C_{16}, C_8, C_6, C_4, C_2$

The cyclohexyleicosanes were prepared by complete hydrogenation at 150–200° over U. O. P. nickel[5] of the phenyl olefins synthesized as above.

Table I summarizes the important properties of the hydrocarbons. The methods of determining the properties listed and their precision and accuracy were discussed in the first paper.[2] Numerous other properties have been determined and will be reported in the appropriate journals.

Experimental

Intermediates.—As emphasized in our earlier papers,[2] great care has been exercised in obtaining pure intermedi-

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[1] American Petroleum Institute Project No. 42: Advisory Committee: L. C. Beard, Jr. (Chairman), J. R. Bates, L. M. Henderson, L. A. Mikeska, H. Ramser and S. Tymstra. Presented before the Organic Division, American Chemical Society, New York, 1944.

[2] Whitmore, Sutherland and Cosby, THIS JOURNAL, **64**, 1360 (1942); Whitmore, Cosby, Sloatman and Clarke, *ibid.*, **64**, 1801 (1942); Whitmore, Herr, Clarke, Rowland and Schiessler, *ibid.*, **67**, 2059 (1945).

[3] Present address: Interchemical Corporation, New York, N. Y.

[4] Present address: Allied Chemical Corporation, Morristown, N. J.

[5] Supplied by the Universal Oil Products Co., Chicago, Ill.

TABLE I

THE PROPERTIES OF THE PHENYL- AND CYCLOHEXYLEICOSANES, $C_{26}H_{46}$ AND $C_{26}H_{52}$

Eicosane	M. p., °C.	B. p. at 1.0 mm., °C.	$n^{20}D$	d^{20}	Viscosity at 20° (centipoises)	*MR* Found	*MR* Calcd.
2-Phenyl-	29.0	204.5	1.4795^a	0.8550^b	20.1^b	119.0	118.7
3-Phenyl-	29.3	201.5	1.4796^a	.8549^b	21.7^b	118.9	118.7
4-Phenyl-	31.4	199.0	1.4794^a	.8548^b	23.9^b	119.0	118.7
5-Phenyl-	30.2	197.0	1.4796^a	.8548^b	25.0^b	118.9	118.7
7-Phenyl-	16.4	196.0	1.4794	.8537	24.68	119.0	118.7
9-Phenyl-	17.9	196.0	1.4790	.8532	23.76	119.0	118.7
2-Cyclohexyl-	13.1	207.0	1.4640	.8371	27.94	120.2	120.1
3-Cyclohexyl-	22.7	205.0	1.4642^a	.8385	26.29	119.9	120.1
4-Cyclohexyl-	16.0	201.5	1.4639	.8382	29.10	120.1	120.1
5-Cyclohexyl-	−2.2	201.5	1.4638	.8373	30.43	119.9	120.1
7-Cyclohexyl-	Glass	199.5	1.4635	.8369	29.49	119.9	120.1
9-Cyclohexyl-	Glass	199.0	1.4635	.8370	27.90	119.9	120.1

[a] Supercooled sample. [b] Extrapolated value.

ates, thus minimizing the difficulties encountered in purification of the final hydrocarbons. Where possible, fractional distillation columns rated at 35–40 theoretical plates have been used. The boiling points of the intermediates are from uncorrected thermometer readings. The constants given are for the constant boiling point, constant refractive index fractions.

(a) **Bromobenzene.**—Eastman Kodak Company practical bromobenzene was carefully fractionated: b. p. 155.5° (732 mm.); $n^{20}D$ 1.5598.

(b) ***n*-Butyl Bromide.**—This was prepared from *n*-butyl alcohol by the hydrobromic–sulfuric acid method. Fractional distillation through a 35-plate column gave the pure product: b. p. 100° (740 mm.); $n^{20}D$ 1.4392.

(c) ***n*-Hexyl Bromide.**—Dry hydrogen bromide gas[6] was bubbled into *n*-hexyl alcohol held at 100–110°. The crude bromide was washed twice with half its volume of cold concentrated sulfuric acid, twice with water, and dried over anhydrous calcium chloride and anhydrous potassium carbonate. After fractional distillation through a 35-plate column, a 75% yield of pure product was collected: b. p. 154° (729 mm.); $n^{20}D$ 1.4478.

(d) ***n*-Octyl Bromide.**—*n*-Octyl bromide was prepared in 80% yield as under *n*-hexyl bromide: b. p. 111° (47 mm.); $n^{20}D$ 1.4527.

(e) **Cetyl Bromide.**—Cetyl bromide was prepared from Eastman Kodak Co. practical cetyl alcohol by the dry hydrogen bromide method (see above) in 73% yield. After fractional distillation through a 35-plate column: b. p. 178° (9 mm.); $n^{20}D$ 1.4620.

(f) ***n*-Octadecyl Bromide.**—*n*-Octadecyl bromide was prepared from Eastman Kodak Co. octadecyl alcohol in 73% yield by the dry hydrogen bromide method (see above), and fractionally distilled through a 35-plate column: b. p. 175° (2 mm.); m. p. 27.4–27.6°; $n^{30}D$ 1.4594; d^{20} 0.9771.

(g) **Acetophenone.**—Eastman Kodak Co. white label acetophenone was fractionally distilled: b. p. 95° (18 mm.); $n^{20}D$ 1.5340.

(h) **Butyrophenone.**—Crude butyrophenone prepared by the Friedel–Crafts reaction of butyryl chloride with benzene in the presence of aluminum chloride was washed with water and 10% sodium hydroxide and dried over anhydrous calcium chloride. After fractional distillation: b. p. 130° (34 mm.); $n^{20}D$ 1.5204.

(i) **Stearonitrile.**—This chemical was obtained from Armour and Company and after fractional distillation through the high vacuum column,[9] constant boiling, constant melting material was obtained: b. p. 184° (2 mm.); m. p. 42.5–43.0°.

(j) **Methyl Laurate, Methyl Myristate and Methyl Palmitate.**—The esters were prepared by the methanolysis of coconut oil and bayberry wax, as outlined in the first paper of this series.[2] After purification through 35-plate fractional distillation columns, material having the following properties was collected: methyl laurate, b. p. 140° (15 mm.), $n^{20}D$ 1.4320; methyl myristate, b. p. 140° (5 mm.), $n^{20}D$ 1.4369, m. p. 19°; methyl palmitate, b. p. 163° (5 mm.), m. p. 29.0–29.3°.

(k) **Acids.**—Lauric, myristic and plamitic acids were prepared in almost quantitative yields from the saponification of the pure methyl esters: lauric acid, m. p. 44°; myristic acid, m. p. 54°; palmitic acid, m. p. 63°.

(l) **Nitriles.**—Pure lauro-, myristo- and palmitonitriles were prepared in 75, 83 and 67% yields, respectively, by the procedure of Ralston, Harwood and Pool,[7] in which dry ammonia gas is passed through the molten acid at 290–300°. The nitriles were distilled through 35-plate fractionating columns: lauronitrile, b. p. 160° (30 mm.), f. p. 3.9°; myristonitrile, b. p. 203° (50 mm.), $n^{20}D$ 1.4410; palmitonitrile, b. p. 156° (3 mm.), f. p. 31°.

SYNTHESIS OF NITRILES

$$R\text{—}CO_2\text{—}CH_3 \xrightarrow[\text{and acidification}]{\text{Saponification}} R\text{—}CO_2H \xrightarrow[290\text{–}300°]{NH_3\ \text{gas}^{7a}} R\text{—}CN + H_2O$$

where R = C_{11}, C_{13} or C_{15}.

(m) **Phenyl Ketones.**—Laurophenone, myristophenone, palmitophenone and stearophenone were prepared by adding lauro-, myristo-, palmito- and stearo-nitriles, respectively, to a slight excess of phenylmagnesium bromide in runs of 1.5 to 2.0 moles. The addition complex was then decomposed with ice and dilute hydrochloric acid, and the ketone recrystallized from ether and methanol: yields of pure ketone, 75–90%.

The oximes of the ketones were prepared by heating a mixture of the ketone, hydroxylamine hydrochloride, 20% sodium hydroxide and ethanol in a glass bomb tube overnight at 100°. The melting points of the ketones and their oximes are recorded in Table II.

TABLE II

THE PHENYL KETONES AND THEIR OXIMES

Ketone	M. p., °C.	M. p. of oxime, °C.
Laurophenone	44	63–63.5
Myristophenone	52.5	69.5–70
Palmitophenone	59	73.5–74.5
Stearophenone	64	79–79.5

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(6) The hydrogen bromide was prepared in a special apparatus to be described in a separate publication.

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

(7a) Unsuccessful attempts were made to carry out this step with the ester in place of the acid.

2-Phenyleicosane and 2-Cyclohexyleicosane.—In the usual apparatus, octadecylmagnesium bromide was prepared in 98% yield from 750 g. (2.25 moles) of *n*-octadecyl bromide and 56 g. (2.25 moles) of magnesium turnings in 1100 ml. of anhydrous ethyl ether. To this was added 288 g. (2.4 moles) of acetophenone dissolved in 500 cc. of anhydrous ether. After stirring overnight, the addition complex was decomposed by pouring into ice–hydrochloric acid mixture, with stirring. After separation, the ether solution was dried over anhydrous potassium carbonate and the ether distilled off. The crude carbinol was dehydrated by heating to 180° over copper sulfate, and the olefin mixture passed through a column of anhydrous 80–200 mesh silica gel.[8]

The resulting olefin mixture, 896 g., was fractionally distilled through a special high vacuum column[9] at 0.3–0.6 mm., and 644 g. of olefin was collected a 75% yield. A portion of the olefin product, 275 g. (0.77 mole) was selectively hydrogenated to 2-phenyleicosane over Raney nickel catalyst at 87° and 1600 lb. per sq. in. hydrogen pressure in nine hours. The hydrogenated product was treated with silica gel to remove the hydrogenation catalyst and any residual polar impurities, after which 245 g. was fractionally distilled through the high vacuum column.[9] Over 95% of the product gave constant boiling point, constant refractive index fractions. The viscosities[10] of the fractions were determined and only those constant to within ±0.3% were accepted and combined as pure 2-phenyleicosane; yield of high purity hydrocarbon, 218 g., 0.60 mole.

For the preparation of **2-cyclohexyleicosane**, 358 g. (1.0 mole) of 2-phenyleicosenes prepared above were completely hydrogenated at 185° and 2300 lb. per sq. in. hydrogen pressure over U. O. P. nickel[5] catalyst in five hours. The 364-g. product was passed through a silica gel adsorption tube and fractionally distilled through the high vacuum column[9] at 0.5 mm., collecting over 99% of the material as constant boiling point, constant refractive index fractions. The viscosities of the fractions at 20.0° were determined, and those constant to within ±0.3% were combined and accepted as pure 2-cyclohexyleicosane; yield of high purity hydrocarbon, 311 g., 0.85 mole.

The above general procedure was employed in the preparation of the rest of the phenyl- and cyclohexyleicosanes, therefore the following preparations are given only in outline.

3-Phenyleicosane.—The crude 3-phenyl-3-eicosanol obtained from the reaction of 2.5 moles of ethylmagnesium bromide with 1.8 moles of stearophenone (added in benzene solution due to its insolubility in ether) was dehydrated over copper sulfate, and the resulting olefins fractionated for a 79% yield. Selective hydrogenation of 152 g. (0.47 mole) gave 135 g. (0.38 mole) of constant boiling point, constant refractive index material, which was accepted as 3-phenyleicosane.

3-Cyclohexyleicosane.—Complete hydrogenation of 172 g. (0.47 mole) of the 3-phenyleicosenes prepared as above gave 150 g. (0.41 mole) of constant boiling point, constant index material accepted as pure 3-cyclohexyleicosane. An alternate method of preparation, involving the addition of phenylmagnesium bromide to 3-eicosanone, yielded a cyclohexyl product having the same index of refraction.

4-Phenyleicosane.—4-Phenyl-4-eicosanol was prepared from 1.25 moles of cetylmagnesium bromide and 1.1 moles of butyrophenone. A 73% yield of olefin was realized. Selective hydrogenation of 240 g. (0.67 mole) of the olefin produced 155 g. (0.43 mole) of pure, constant viscosity, constant boiling, constant index hydrocarbon.

4-Cyclohexyleicosane.—4-Cyclohexyleicosane was obtained by complete hydrogenation of 300 g. (0.85 mole) of the 4-phenyleicosenes from the above preparation. A yield of 213 g. (0.58 mole) of pure, constant viscosity 4-cyclohexyleicosane was realized.

5-Phenyleicosane.—The hydrocarbon was obtained from the reaction of 1.5 moles of *n*-butylmagnesium bromide and 0.9 mole of palmitophenone. A 78% yield of olefinic product resulted from the dehydration of the tertiary alcohol. Selective hydrogenation of 225 g. (0.63 mole) of the phenyleicosenes gave 182 g. (0.51 mole) of pure 5-phenyleicosane after fractional distillation.

5-Cyclohexyleicosane.—Complete hydrogenation of 245 g. (0.69 mole) of the 5-phenyleicosenes prepared as above produced 142 g. (0.39 mole) of pure hydrocarbon. The low yield is attributed to the loss involved on rehydrogenation.

7-Phenyleicosane.—The hydrocarbon was prepared from the carbinol resulting from the reaction of 2.3 moles of *n*-hexylmagnesium bromide and 1.7 moles of myristophenone. An 85% yield of fractionally distilled olefin was obtained. Selective hydrogenation of 195 g. (0.55 mole) gave 145 g. (0.40 mole) of pure 7-phenyleicosane following fractional distillation.

7-Cyclohexyleicosane.—From the complete hydrogenation 194 g. (0.55 mole) of the 7-phenyleicosenes prepared as above. A yield of 145 g. (0.40 mole) of pure hydrocarbon was obtained.

9-Phenyleicosane.—A tertiary alcohol was synthesized by the reaction of 1.8 moles of *n*-octylmagnesium bromide and 1.86 moles of laurophenone. A yield of 90% of fractionally distilled olefin was obtained from the dehydration product of the tertiary carbinol. Selective hydrogenation of 209 g. (0.59 mole) of the olefins gave 184 g. (0.51 mole) of pure 9-phenyleicosane.

9-Cyclohexyleicosane.—From the complete hydrogenation of 265 g. (0.74 moles) of the 9-phenyleicosenes prepared by the dehydration of 9-phenyl-9-eicosanol. A yield of 186 g. (0.51 mole) of pure hydrocarbon was realized.

Acknowledgment.—The authors express their appreciation to the American Petroleum Institute for the grant which made this research possible.

Summary

1. The methods of preparation, yields and five important properties of six phenyleicosanes and six cyclohexyleicosanes are reported.
2. Data on the preparations, yields and properties of twenty intermediates are given.

STATE COLLEGE, PENNA. RECEIVED AUGUST 20, 1946

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[8] Supplied by the Davison Chemical Co., Baltimore, Md.

[9] Nine to ten theoretical plates. To be described in a separate publication to be submitted to the *Analytical Edition* of *Industrial and Engineering Chemistry*.

[10] The importance and sensitivity of the viscosity method of determination of the uniformity of composition of fractions will be the subject of a separate publication