Recrystallization from benzene–petroleum ether mixture (1:1) gave 0.3 g. (30%) of VIIIa as pale yellow needles, m.p. 197–200°.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.4; H, 6.1. Found: C, 88.9; H, 6.6.

Action of ethylmagnesium iodide on IV. A solution of 2,4-diphenyl-5,6-benzindan-1,3-dione (IV) (1 g.) in dry benzene (100 ml.) was added to an ethereal solution of ethylmagnesium iodide (from ethyl iodide, 3.5 g., and magnesium, 0.5 g.) and the reaction mixture was heated under reflux for 2 hr., then left overnight. Decomposition with aqueous ammonium chloride solution, and concentration of the washed and dried benzene extracts, gave a pale yellow product. Recrystallization from benzene gave 0.25 g. (24%) of IX as almost colorless needles, m.p. 182–184°.

Anal. Calcd. for $C_{29}H_{24}$: C, 93.5; H, 6.5. Found: C, 92.8; H, 6.4.

The product gave a rose red coloration with concentrated sulfuric acid.

Action of phenylmagnesium bromide on IV. A solution of 2,4-diphenyl-5,6-benzindan-1,3-dione (IV) (1 g.) in dry benzene (100 ml.) was added to an ethereal solution of phenylmagnesium bromide (from bromobenzene, 2 g., and magnesium, 0.5 g.) and the reaction mixture was heated under reflux for 3 hr. then left overnight. Decomposition with aqueous ammonium chloride solution, and concentration of the washed and dried benzene extracts followed by addition of petroleum ether (40–60°), gave a colorless product. Recrystallization from benzene–petroleum ether mixture (1:1) gave 0.4 g. (30%) of VIIIb as colorless prisms, m.p. 198–199°.

Anal. Calcd. for $C_{37}H_{26}O$: C, 91.3; H, 5.4. Found: C, 91.1; H, 5.4.

The product gave a bluish coloration with concentrated sulfuric acid.

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ABBASSIA, CAIRO, EGYPT

[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY]

Higher Hydrocarbons. VI.[1] Polyalkylbenzenes and Polyalkylcyclohexanes[2]

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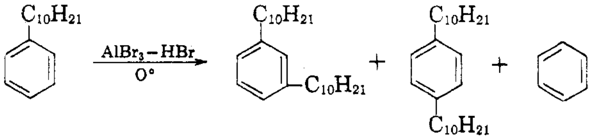
The syntheses of six new high molecular weight polyalkylbenzenes and polyalkylcyclohexanes are reported.

As a portion of a continuing study of high molecular weight hydrocarbons, the synthesis and physical properties of six new monocyclic hydrocarbons are reported. They are 1,3-didecylbenzene, 1,3-didecylcyclohexane, 2,5-dimethyloctadecylbenzene, 2,5-dimethyloctadecylcyclohexane, 2,4,6-trimethyloctadecylbenzene, and 2,4,6-trimethyloctadecylcyclohexane.

Three different synthetic routes were used for the preparations of the above hydrocarbons. The 1,3-didecylbenzene was prepared by the disproportionation of decylbenzene with aluminum bromide–hydrogen bromide catalyst.[3–6]



It has been found from studies of the hydrogen fluoride and aluminum halide catalyzed disproportionations of a series of lower alkylbenzenes that the dialkylbenzenes obtained are exclusively the meta isomers except in the case of isopropyl or tertiary butylbenzene.[3,4] It was believed that the increased branching of the alkyl group in these two cases decreased the differences in the stability of the isomeric hydrocarbon catalyst complexes.[5] In the present work it was observed that the disproportionation of decylbenzene catalyzed by aluminum chloride–hydrogen chloride yielded a four to one ratio of *meta-* to *para-*didecylbenzene while aluminum bromide–hydrogen bromide produced the isomers in a nine to one ratio. The ortho isomer was looked for but not found. Analysis was by infrared, density, and viscosity, after separation of the isomers by fractional distillation. The identity of the para isomer was unequivocally established by comparison with an authentic sample which had been prepared previously in this labora-

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[1] For the previous paper in this series: R. W. Schiessler, A. W. Rytina, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 529 (1948).

[2] Taken from a portion of a dissertation submitted by S. G. Clark to the Graduate School of The Pennsylvania State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. P. Lien and D. A. McCaulay, *J. Am. Chem. Soc.*, **75**, 2407, 2411 (1953).

[4] R. D. Kinney and L. A. Hamilton, *J. Am. Chem. Soc.*, **76**, 786 (1954).

[5] H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 2176 (1956).

[6] R. M. Roberts and S. G. Brandenberger, *J. Am. Chem. Soc.*, **79**, 5485 (1957).

TABLE I

PROPERTIES OF THE HYDROCARBONS

Hydrocarbon	Viscosity at 98.9° C. (Centipoise)	Density in G./Cc. at 98.9°C.	B.P. at 1.00 Mm., °C.	Refractive Index ($n^t_{\rm D}$), 20° C.	M.P., °C.
1,3-Didecylbenzene	2.496	0.8018	201.0	1.4813	—
1,3-Didecylcyclohexane	2.863	0.7816	205.0	1.4618	—
2,5-Dimethyloctadecylbenzene	2.887	0.8078	210.5	Solid	45.0–45.5
2,5-Dimethyloctadecylcyclohexane	2.963	0.7829	204.0	1.4619	—
2,4,6-Trimethyloctadecylbenzene	3.580	0.8125	219.0	Solid	54.5–55.0
2,4,6-Trimethyloctadecylcyclohexane	3.268	0.7856	210.5	1.4629	—

tory from terephthalic acid.[7] This also confirmed the previous observations[3–5] that the disproportionation is not accompanied by isomerization of the normal alkyl group.

For the synthesis of 2,5-dimethyloctadecylbenzene the precursor, 2,5-dimethyloctadecanoylbenzene, was prepared both by the acylation of *p*-xylene with stearoyl chloride, and from 2,4-dimethylbrombenzene and octadecanoyl chloride through the Grignard and cadmium reagents. In each case the ketone was reduced directly to the hydrocarbon by the modified Wolff-Kishner reaction of Herr *et al.*[8] The Friedel-Crafts acylation is not accompanied by rearrangement of the methyl groups (or by isomerization of the normal octadecyl chain) since the ketones obtained from the two procedures were shown to be identical. The yield of purified ketone from the acylation was 62 per cent and from the Grignard reaction 34 per cent.

The 2,4,6-trimethyloctadecylbenzene was prepared from mesitylene by acylation with octadecanoyl chloride, reduction with lithium aluminum hydride, dehydration over alumina at 350° and finally hydrogenation over copper chromite catalyst. The best commercial mesitylene contained a hydrocarbon impurity boiling within a few degrees of the desired 1,3,5-trimethylbenzene. A fractionating column possessing 100 theoretical plates was required to separate this impurity which from physical property data appeared to be a methylethylbenzene. Attempts at direct reduction of the ketone to the hydrocarbon *via* the Clemmensen[9] or the Wolff-Kishner[10] methods were unsuccessful. In each case the ketone was recovered unchanged, apparently because of the steric hindrance of the ortho methyl groups.

The 1,3-didecylcyclohexane and 2,5-dimethyloctadecylcyclohexane were prepared by complete hydrogenation of the respective aromatic analogs over a nickel catalyst[11] at 150–200°. The 2,4,6-trimethyloctadecylcyclohexane was prepared by complete hydrogenation of 1-(2,4,6-trimethylphenyl)-1-octadecene.

The cyclohexane derivatives are mixtures of geometric isomers and the properties given were determined on these mixtures.

Several of the important physical properties determined for the hydrocarbons are listed in Table I. The methods of determining the properties and their precisions were discussed in the first paper of the series.[12]

EXPERIMENTAL[13]

Intermediates. Careful purification of the intermediates greatly simplifies the purification of the final hydrocarbons. Where possible, all intermediates were fractionally distilled through distillation columns having at least 35–40 theoretical plates. The boiling points of the intermediates are uncorrected unless otherwise specified. The properties listed are for the fractions having similar boiling points, refractive indices, and melting points or viscosities.[14]

(a) *Decanoic acid.* Capric acid (Armour Neo-Fat 10) was purified by fractional distilllation: b.p. 168°/28 mm., setting point found 31.3°; reported[15] 31.24°.

(b) *Octadecanoic acid.* Stearic acid (Armour Neo-Fat 18) was converted to methyl stearate which was purified by fractional distillation through a "solids high vacuum column:"[16] $Z^{37.8}$ 5.984 cs. The ester was converted to the acid by saponification with aqueous sodium hydroxide, followed by acidification with dilute hydrochloric acid: m.p. found 69.0–69.6°, reported[15] 69.60°.

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(7) R. W. Schiessler, F. C. Whitmore, J. A. Dixon, J. N. Cosby, W. P. Acton, D. G. Clarke, W. K. Conn, R. C. East, N. R. Eldred, F. B. Fischl, David Flitter, E. J. Goldberg, C. H. Herr, J. F. Hosler, F. T. Kerr, H. H. Kuehner, R. L. McLaughlin, P. C. Miller, G. W. Pearce, C. S. Rowland, A. W. Rytina, W. S. Sloatman, R. M. Speck, L. H. Sutherland, and C. A. Weisel, *Ind. Eng. Chem.*, **47**, 1660 (1955).

(8) C. H. Herr, R. W. Schiessler, and F. C. Whitmore, *J. Am. Chem. Soc.*, **67**, 2061 (1945).

(9) E. L. Martin, *Org. Reactions*, **I**, 166 (1942).

(10) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(11) A kieselguhr-supported nickel supplied by the Universal Oil Products Co., Chicago, Ill.

(12) F. C. Whitmore, L. H. Sutherland, and J. N. Cosby, *J. Am. Chem. Soc.*, **64**, 1360 (1942).

(13) Microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(14) Only those fractions whose viscosities agreed within 0.3% were combined as high purity material.

(15) C. W. Ralston, *Fatty Acids and Their Derivatives*, John Wiley and Sons, New York, 1948, p. 323.

(16) The packed section of this column is 90 cm. long with an inside diameter of 25 mm. and is packed with 0.24 × 0.24 inch protruded metal packing. The efficiency is estimated to be approximately 15 theoretical plates.

(c) *Decanoyl chloride* was prepared by reaction of *n*-decanoic acid with thionyl chloride at 25°. Yield of product obtained upon distillation of the reaction mixture through a Claisen head was 94.7%; b.p. 133°/30 mm.

(d) *Octadecanoyl chloride* was prepared by the reaction of octadecanoic acid with phosphorus pentachloride. The crude acid chloride, after removal by distillation of the phosphorus oxychloride, was used for the subsequent acylations.

(e) *1,4-Dimethylbenzene.* Oronite Chemical Company *p*-xylene was purified by fractional distillation through a glass-helices packed column having 40 theoretical plates: b.p. 138°/745 mm., n_D^{25} 1.4931, Z^{20} 0.748 cs; reported:[17] b.p. 138.35/760 mm.; n_D^{25} 1.49325: Z^{20} 0.748 cs.

(f) *1,3,5-Trimethylbenzene.* Matheson, Coleman and Bell Chemical Co. mesitylene was purified by fractional distillation through a column having 100 theoretical plates: n_D^{25} 1.4967, Z^{20} 0.813 cs, b.p. 164°/24 mm.; reported:[17] n_D^{25} 1.49684.

1,3-Didecylbenzene. Decanoyl chloride (1718 g., 9.01 moles) was stirred with a suspension of anhydrous aluminum chloride (1370 g., 10.27 moles, Allied Chemical and Dye Co.) in thiophene-free benzene (1300 g., 16.7 moles) for 4 hr. at 25°. Hydrolysis over cracked ice followed by distillation of the hydrolysis product through a "solids high vacuum column"[15] gave 1653 grams (78.9%) of nonyl phenyl ketone: m.p. 34.3°, 2,4-dinitrophenylhydrazone, m.p. 108.7–109.2°.

Reduction of the ketone by the modified Wolff-Kishner reaction[7] followed by fractional distillation of the reduction product through a 40 plate column gave 1029 grams (74.1%) of decylbenzene: b.p. 158°/9 mm. n_D^{25} 1.4812, Z^{20} 4.45 cs; reported[7,17] n_D^{25} 1.48112, Z^{20} 4.44. The infrared spectrum was identical with an authentic sample kindly supplied by Professor Cecil Boord of the Ohio State University. A typical disproportionation was conducted as follows: Decylbenzene (253.2 g., 1.16 moles) and aluminum bromide (Fisher Scientific Co., 199.1 g., 0.75 mole) were cooled to 0° and anhydrous hydrogen bromide (Matheson Co., 29.9 g., 0.37 mole) was bubbled into the hydrocarbon–aluminum bromide mixture while stirring. The mixture was stirred for 40 hr. at 0° to yield a mixture of benzene, decylbenzene, 1,3-didecylbenzene and a small quantity of 1,4-didecylbenzene. Fractional distillation of the disproportionation product through a spinning band column[18] gave a 48.1% yield of high purity 1,3-didecylbenzene: (See Table I for properties).

Anal. Calcd. for $C_{26}H_{46}$: C, 87.07; H, 12.93. Found C, 87.25; H, 12.96.

1,3-Didecylcyclohexane. Hydrogenation of 1,3-didecylbenzene (208.0 g., 0.58 mole) over a nickel catalyst[11] (10% by weight) at 150° and 1900 p.s.i. gave 199.5 grams (94.3%) of 1,3-didecylcyclohexane: (See Table I for properties).

Anal. Calcd. for $C_{26}H_{52}$: C, 85.63; H, 14.37; MR, 120.5. Found C, 85.61; H, 14.46; MR, 120.1.

2,5-Dimethyloctadecylbenzene. A solution of aluminum chloride (366.8 g., 2.75 moles) in nitrobenzene (2 l.) was added slowly with stirring to a solution of stearoyl chloride (644.0 g., 2.13 moles) and *p*-xylene (227.2 g., 2.14 moles) in nitrobenzene (1 liter). The reaction mixture was stirred at 0° for 4 hr. After hydrolysis on cracked ice, the organic layer was fractionally distilled through a spinning band column, (b.p. 185°/0.25 mm).[18] After one recrystallization from 95% ethanol the yield of 2,5-dimethyloctadecanoylbenzene was 492.1 grams (62.1%); m.p. 58.0–58.5°.

Anal. Calcd. for $C_{26}H_{44}O$: C, 83.80; H, 11.90. Found C, 84.15; H, 11.64.

Reduction of 2,5-dimethyloctadecanoylbenzene by the modified Wolff-Kishner reaction[8] gave 345.2 grams (72.4%) of 2,5-dimethyloctadecylbenzene: (See Table I for properties).

Anal. Calcd. for $C_{26}H_{46}$: C, 87.07: H, 12.93. Found: C, 87.13; H, 12.94.

2,5-Dimethyloctadecylcyclohexane. Hydrogenation of 2,5-dimethyloctadecylbenzene (294.0 g., 0.82 mole) over a nickel catalyst[11] (10% by weight) at 200° and 2500 p.s.i. gave 289.2 grams (96.5%) of 2,5-dimethyloctadecylcyclohexane: (See Table I for properties).

Anal. Calcd. for $C_{26}H_{52}$: C, 85.63; H, 14.37; MR, 120.4. Found: C, 85.75; H, 14.35; MR, 120.1.

2,4,6-Trimethyloctadecylbenzene. Acylation of 1,3,5-trimethylbenzene (144.2 g., 1.2 moles) with stearoyl chloride (365.5 g., 1.2 moles), following the procedure described for the acylation of 1,4-dimethylbenzene gave 346.5 grams (74.3%) of 2,4,6-trimethyloctadecanoylbenzene: b.p. 178°/0.23 mm., m.p. 50.9–51.5°.

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C, 83.71; H, 11.99.

2,4,6-Trimethyloctadecanoylbenzene (489.2 g., 1.26 moles) was reduced to the corresponding alcohol by stirring with lithium aluminum hydride (17.8 g., 0.47 mole, Metal Hydrides, Inc.) in anhydrous diethyl ether at the reflux temperature for 20 hr. After decomposition of the excess hydride by slow addition of an ether-methanol-water (1:1:1) solution and coagulation of the aluminum hydroxide by refluxing for an hour the ether solution was decanted. The alcohol was obtained as white needles by cooling the ether solution to −10°. The yield of 1-(2,4,6-trimethylpentyl)-1-octadecanol was 478.1 grams (97.6%); m.p. 61.5–62.0°. The alcohol was dehydrated to 1-(2,4,6-trimethylphenyl)-1-octadecene in 98.0% yield by passage over activated alumina at 340–360° and *ca.* 1 mm. pressure. Hydrogenation of the olefin over copper chromite catalyst (10% by weight) at 150° and 2000 p.s.i. gave a 96.5% yield of 2,4,6-trimethyloctadecylbenzene. The hydrocarbon was purified by one crystallization from hexane: (See Table I for properties).

Anal. Calcd. for $C_{27}H_{48}$: C, 87.02; H, 12.98. Found: C, 86.81; H, 13.03.

2,4,6-Trimethyloctadecylcyclohexane. Hydrogenation of 1-(2,4,6-trimethylphenyl)-1-octadecene (397.3 g., 1.07 moles) over a nickel catalyst[11] (10% by weight) at 195° and 1650 p.s.i. gave 394.3 grams (97.3%) of 2,4,6-trimethyloctadecylcyclohexane: (See Table I for properties).

Anal. Calcd. for $C_{27}H_{54}$: C, 85.63; H, 14.37; MR, 125.0. Found: C, 85.51; H, 14.26; MR, 124.7.

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(17) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimental, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, Pa., 1953.

(18) This column is manufactured by the Nester-Faust Co., Exton, Pa. The packed section is three feet long with an internal diameter of 11 mm. The band is a spiral of 300 mesh stainless steel screen.