

methallyl polymers were hard, colorless, insoluble and infusible and the benzyl and tetra-

hydrofurfuryl polymers were hard and colorless. PHILADELPHIA 18, PA. RECEIVED AUGUST 8, 1947

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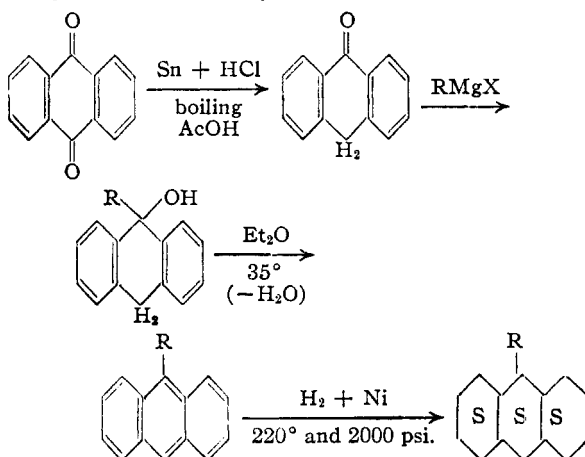
Higher Hydrocarbons.¹ V.² Alkyl Anthracenes and Alkyl Phenanthrenes

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As part of our studies of the synthesis, purification and properties of high molecular weight hydrocarbons, the preparations of several alkyl-anthracenes and -phenanthrenes, together with the corresponding perhydro derivatives, have been completed. They are 9-*n*-butylanthracene, 9-*n*-butylperhydroanthracene, 9-*n*-dodecylanthracene, 9-*n*-dodecylperhydroanthracene, 9-*n*-dodecylphenanthrene and 9-*n*-dodecylperhydrophenanthrene.

The alkyl anthracenes were synthesized by a modification of the method of Sieglitz and Marx.³ The method consists of the addition of anthrone to alkylmagnesium halides, followed by dehydration of the resultant tertiary alcohol to the desired alkyl anthracene:

Synthesis of 9-Alkylanthracenes.—



9-*n*-Dodecylphenanthrene was prepared by the addition of lauronitrile^{2,4} to 9-phenanthrylmagnesium bromide⁵ followed by reduction of the resulting 9-phenanthryl hendecyl ketone to the hydrocarbon by the modified Wolff-Kishner method.⁶

(1) American Petroleum Institute Research Project No. 42; Advisory Committee: L. C. Beard, Jr. (Chairman), J. R. Bates, L. M. Henderson, R. G. Larsen, R. F. Marchner, L. A. Mikeska, J. H. Ramser.

(2) Whitmore, Sutherland and Cosby, *THIS JOURNAL*, **64**, 1360 (1942); Whitmore, Cosby, Sloatman and Clarke, *ibid.*, **64**, 1810 (1942); Whitmore, Herr, Clarke, Rowland and Schiessler, *ibid.*, **67**, 2059 (1945); Whitmore, Schiessler, Rowland and Cosby, *ibid.*, **69**, 225 (1947).

(2a) Deceased, June 24, 1947.

(3) Sieglitz and Marx, *Ber.*, **56**, 1619 (1923).

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

(5) Bachmann, *ibid.*, **56**, 1365 (1934).

(6) Whitmore, Herr, Clarke, Rowland and Schiessler, *ibid.*, **67**, 2059 (1945).

The perhydro derivatives of the hydrocarbons were prepared by complete hydrogenation over nickel catalyst⁷ at 100–230° and 2300 p.s.i. hydrogene pressure.

It must be emphasized that the perhydro derivatives reported are mixtures of geometric isomers, and the properties given were determined on these mixtures of unknown composition. The difficulty of separating and identifying the various *cis-trans* structures precludes following any other course for our work.

Several of the important physical properties of the hydrocarbons are listed in Table I. The methods of determining the properties and their precision were discussed in the first paper of the series.² Numerous other properties have been determined and will be reported in the appropriate journals.

Experimental

Intermediates.—In order to simplify the purification of the final hydrocarbons, great care has been taken with the purification of intermediates. Where possible, distillation of intermediates through fractionating columns of 35–40 theoretical plates was carried out. The boiling points of the intermediates are uncorrected. The properties listed are for the constant boiling, constant refractive index fractions.

(a) *n*-Butyl Bromide.—Edwal Laboratories *n*-butyl bromide was carefully fractionated: b. p. 100° (733 mm.); *n*_D²⁰ 1.4392.

(b) Lauryl bromide⁸ was prepared by passing hydrogen bromide (from the direct combination of bromine and hydrogen) into Eastman Kodak Company technical lauryl alcohol at 120°. After washing twice with half its volume of cold (0–5°), concd. sulfuric acid and then with an equal volume of 95% methanol, the crude lauryl bromide was dried over anhydrous potassium carbonate and fractionally distilled through a 35–40 plate all glass column. The yield of pure bromide was 50% from this crude alcohol: b. p. 122° (4 mm.); *n*_D²⁰ 1.4586.

(c) Anthrone.—Eastman Kodak Company anthraquinone (highest purity) was reduced to anthrone in 60% yield,⁹ m. p. 156–157°.

(d) 9-Bromophenanthrene.—Reilly Tar & Chemical Co. 90% phenanthrene was purified by the method of Cohen and Carmier¹⁰; m. p. 99.0–99.5°. A total of 508 g. of 9-bromophenanthrene was prepared in 55% yield following Austin¹¹; m. p. 65–66°.

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

(8) Further experience has shown that emulsion difficulty at the sulfuric acid wash step can be obviated by a preliminary simple distillation *in vacuo* of the Eastman Kodak Co. Technical Lauryl Alcohol. A considerable residue is eliminated.

(9) "Organic Syntheses," John Wiley and Sons, New York, N. Y., 1944, Coll. Vol. I, p. 60 (2nd edition).

(10) Cohen and Cormier, *THIS JOURNAL*, **52**, 4363 (1930).

(11) Austin, *J. Chem. Soc.*, **93**, 1762 (1908).

TABLE I
 PROPERTIES OF THE HYDROCARBONS

Hydrocarbon	M. p., °C.	B. p., at 1.00 mm., °C.	d_{20}^{20}	Viscosity at 98.9° (centi- poises)	n_D^{20}	MR	
		Found				Calcd.	
9- <i>n</i> -Butylanthracene	48.9	162.0	1.0007	4.630	Solid	Solid	75.5
9- <i>n</i> -Butylperhydroanthracene	Up to 38.3 ^a	133.5	.8877	3.311	1.5049 ^b	Solid	78.8
9- <i>n</i> -Dodecylanthracene	49.3	236.5	.9256	6.593	Solid	Solid	112.5
9- <i>n</i> -Dodecylperhydroanthracene	Up to 34.5 ^a	214.5	.8522	5.147	1.4911 ^b	Solid	115.7
9- <i>n</i> -Dodecylphenanthrene	75.8	237.0	.9292	5.979	Solid	Solid	112.5
9- <i>n</i> -Dodecylperhydrophenanthrene	Glass	213.0	.8571	5.134	1.4931	Solid	115.7

^a Melting was complete at this temperature. ^b Supercooled sample. ^c Corrected for air buoyancy.

(e) **Lauroitrile.**—Prepared by the passage of ammonia through molten lauric acid (from the saponification of pure methyl laurate; m. p. of acid 44–44.5°) in 70% yield as described previously,^{2,4} except that a few ml. of 85% phosphoric acid was added as a catalyst, substantially reducing the reaction time.¹²

9-*n*-Dodecylanthracene.—A Grignard solution was prepared in the usual manner from 1668 g. (6.7 moles) of lauryl bromide and 163 g. (6.7 moles) of magnesium in 92% yield, using 3.5 l. of diethyl ether as a solvent. An ether suspension of 368 g. (2.0 moles) of anthrone was added to this solution at 15°. After stirring for ten hours the reaction products were poured on a mixture of 1100 g. of ammonium sulfate and 1500 g. of ice with stirring. The ether layer was removed by distillation and the residue dissolved in 1200 ml. of toluene. The toluene solution was extracted exhaustively with 3% aqueous sodium hydroxide until the extracts were colorless. The toluene was distilled off and the residue dissolved in 1200 ml. of purified pentane, which was then passed successively through four 80 × 2 cm. columns of silica gel.¹³ Upon evaporation of the pentane, 375 g. (49.5% yield) of crude hydrocarbon melting at 48–49° was obtained. The crude product was fractionally distilled through the high vacuum column¹⁴ at 0.5 mm., yielding 371 g. of constant viscosity¹⁵ constant melting 9-*n*-dodecylanthracene (see Table I).

9-*n*-Butylanthracene was prepared from *n*-butylmagnesium bromide and anthrone in the same manner as under 9-*n*-dodecylanthracene above. A total of 360 g. (43% yield) of constant melting, constant viscosity¹⁵ hydrocarbon was obtained (refer Table I) after fractional distillation at high vacuum.¹⁴

9-*n*-Dodecylphenanthrene.—A Grignard reagent was prepared in 95% yield from 508 g. (1.98 moles) of 9-bromophenanthrene and 48.1 g. (1.98 moles) of magnesium turnings in a mixture consisting of 500 ml. of diethyl ether and 500 ml. of benzene. To this solution was added 293 g. (1.61 moles) of lauroitrile at reflux temperature. After stirring for sixteen hours the reaction product was decomposed with 110 ml. of concd. sulfuric acid, and 1500 g. of ice. The organic layer was dried by distillation of the solvents and yielded 465 g. of 9-phenanthryl hendecyl ketone: 80% yield; m. p. 72–73°; 2,4-dinitrophenylhydrazone m. p. 145.0–145.5°. The ketone was reduced in 0.5 mole portions by the modified Wolff-Kishner

method,⁶ yielding a total of 415 g. of 9-dodecylphenanthrene in 73% yield: m. p. 78–79° (mixed m. p. with 9-phenanthryl hendecyl ketone 65–71°). To ensure the complete removal of ketone, the hydrocarbon was treated with 0.5 mole of phenylmagnesium bromide. After decomposition with dilute sulfuric acid, drying over anhydrous potassium carbonate, and removal of the solvent, the hydrocarbon was treated with silica gel¹³ in pentane solution and fractionated through the high vacuum column¹⁴ to yield 408 g. of constant melting, constant viscosity¹⁵ 9-*n*-dodecylphenanthrene (refer Table I).

9-*n*-Dodecylperhydroanthracene.—Prepared as a mixture of stereoisomers by the hydrogenation of 237 g. of pure 9-*n*-dodecylanthracene over 20 g. of nickel catalyst⁷ at 100–230° and 2250–1000 p. s. i. of hydrogen pressure. In order to ensure complete hydrogenation, the crude material was passed through a train of silica gel¹³ and fractionated through the high vacuum column.¹⁴ The material boiling at 176–182° (0.3 mm.), 226 g., was rehydrogenated and treated as above to yield 218 g. of hydrocarbon boiling at 174° (0.1 mm.). The product was then passed through a column of activated silica gel¹³ to remove traces of polar impurities.

9-*n*-Butylperhydroanthracene.—Hydrogenation of 155 g. of pure 9-*n*-butylanthracene employing the same method as listed above in three successive steps to ensure complete hydrogenation, yielded 141 g. of purified hydrocarbon after high vacuum fractionation,¹⁴ boiling at 105° (0.3 mm.); n_D^{20} 1.5048–50 (supercooled sample). The product is a mixture of stereoisomers, and was given a final treatment with silica gel¹³ to remove traces of polar impurities.

9-*n*-Dodecylperhydrophenanthrene.—Prepared by the three-step hydrogenation of 218 g. of pure 9-dodecylphenanthrene over nickel catalyst⁷ at 2600–1500 p. s. i. and 100–225°. The mixture of *cis-trans* isomers obtained from the third fractionation through the high vacuum column¹⁴ boiled at 178° (0.2 mm.); n_D^{20} 1.4926; 203 g. A final silica gel treatment was employed as described above.

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Summary

1. The methods of preparation, yields, and five important properties are given for two alkyl anthracenes, one alkyl phenanthrene, and the corresponding perhydro derivatives. The aromatic hydrocarbons are pure, but the perhydro derivatives are known to be mixtures of *cis-trans* isomers.

2. Data on the preparation, yields and properties of six intermediates are given.

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(12) R. W. Schiessler and R. L. McLaughlin of these laboratories discovered the catalytic efficiency of phosphoric acid or silica gel for this reaction. Reaction time is reduced by approximately 50%, and ease of manipulation is increased.

(13) The activated silica gel (28–200 mesh) was supplied by the Davison Chemical Corp., Baltimore, Md.

(14) Nine to ten theoretical plates. To be described in a separate publication to be submitted to *Analytical Chemistry*.

(15) The viscosities of the fractions were determined and only those constant to within $\pm 0.3\%$ were accepted and combined as pure hydrocarbon. The importance and sensitivity of the viscosity method of determining uniformity of composition will be the subject of a separate publication.