(b) **Measurement and Computation.**—Refractive indices, n, were measured on benzene solutions of the substances in an Abbe precision refractometer. The measurement of dielectric constants ϵ and densities d, as well as the computation of the molar refractions and polarizations from the slopes of the lines depicting ϵ, n, and d *versus* weight fraction have been described before.[28] The variations in the approximate error in $R^{D}_{\text{obs.}}$ given in each case are due mainly to differences in the range of the solute concentrations.

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[28] E. D. Bergmann, A. Weizmann and E. Fischer, This Journal, **72**, 5009 (1950); E. Fischer, *J. Chem. Phys.*, **19**, 395 (1951).

Rehovoth and Tel-Aviv, Israel

[Contribution from the Lewis Flight Propulsion Laboratory of the National Advisory Committee for Aeronautics]

Dicyclic Hydrocarbons. VI. 1,2,3,4-Tetrahydronaphthalene and 1-Alkyl-1,2,3,4-tetrahydronaphthalenes

By Wolf Karo, Robert L. McLaughlin and Harold F. Hipsher

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Methods of synthesis and purification as well as physical properties are presented for four 1-alkyl-1,2,3,4-tetrahydronaphthalenes along with the physical properties of 1,2,3,4-tetrahydronaphthalene. The boiling point, refractive index, density, net heat of combustion and kinematic viscosities at four different temperatures are given for each compound. Two compounds, 1-butyl-1,2,3,4-tetrahydronaphthalene and 1-pentyl-1,2,3,4-tetrahydronapthalene, are described for the first time.

In connection with an investigation of aviation fuel components carried out at this Laboratory, several series of dicyclic hydrocarbons have been synthesized and purified. Among the compounds previously described, for example, have been the diphenyl- and dicyclohexylbutanes.[1] For the purpose of correlating the physical properties with molecular structure, it was deemed desirable to extend this study to the fused dicyclic system. The preparation of 1-alkylnaphthalenes has been reported upon earlier.[2] In this paper 1,2,3,4-tetrahydronaphthalene and four of its homologs are described. The latter hydrocarbons are 1-methyl-, 1-ethyl-, 1-butyl- and 1-pentyl-1,2,3,4-tetrahydronaphthalene. Of these, the 1-butyl- and 1-pentyl-compounds are reported for the first time. The other compounds in this series were synthesized in order to obtain a consistent set of precise physical constants on highly purified samples of these structurally related hydrocarbons. Although all of the 1-alkyl-1,2,3,4-tetrahydronaphthalenes are capable of optical activity, no attempt was made to resolve racemic mixtures.

Among the reported syntheses of 1-methyl- and 1-ethyl-1,2,3,4-tetrahydronaphthalene in which the alkyl substitutents are unequivocally attached to the indicated position in the saturated ring portion of the molecule have been those of Darzens[3] and of Bogert, Davidson and Roblin.[4] These procedures involve the formation of the aliphatic ring by the cyclization of a variety of alkyl benzene derivatives of appropriate chain length.

Since it was the object of the present research to prepare the desired hydrocarbons on such a scale that approximately 500-ml. quantities would be available after the final distillation, the ring closure method was not considered a suitable procedure because low over-all yields were anticipated. A synthesis was sought which did not involve the initial preparation of a relatively complex alkyl benzene derivative for each desired hydrocarbon but which instead permitted the use of a single starting material with a preformed fused ring system. An effective synthetic route was found in the method of Hock and Lang[5] modified by substitution of catalytic hydrogenation for the sodium–pentanol reduction used by these authors. Thus, it was possible to prepare the desired homologs of 1,2,3,4-tetrahydronaphthalene conveniently.

The preparation of 1-methyl-, 1-ethyl-, 1-butyl- and 1-pentyl-1,2,3,4-tetrahydronaphthalene involved the reactions of methyl-, ethyl-, butyl- and pentylmagnesium bromide, respectively, with 1-tetralone. The resultant Grignard complexes were decomposed to yield tertiary alcohols, the 1-alkyl-2,3,4-trihydronaphthalene-1-ols. These carbinols were dehydrated to the corresponding olefins. Selective high pressure hydrogenation of the olefinic bond afforded the desired hydrocarbon.

The final purification of the 1-alkyl-1,2,3,4-tetrahydronaphthalenes consisted of fractional distillation of each product in six-foot Podbielniak columns.[6] The individual fractions were percolated through columns of activated silica gel prior to the determination of all physical constants. Only those fractions exhibiting constancy of both refractive index and density were combined for analyses and for the determination of precise physical constants. The physical constants, particularly those which, like the density, exhibit large variation with slight traces of impurities, were measured on samples of the products immediately after final passage through silica gel to obviate the effects of possible air-oxidation.

The parent hydrocarbon of this series, 1,2,3,4-tetrahydronaphthalene, was obtained from commercial sources. This material was fractionally distilled in a 30-foot column two inches in diameter,

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[1] K. T. Serijan and P. H. Wise, This Journal, **74**, 365 (1952).

[2] H. F. Hipsher and P. H. Wise, National Advisory Committee for Aeronautics, Technical Note 2430, Cleveland (1951).

[3] G. Darzens, *Compt. rend.*, **183**, 748 (1926).

[4] (a) M. T. Bogert, D. Davidson and R. O. Roblin, Jr., This Journal, **56**, 248 (1934); (b) R. O. Roblin, Jr., D. Davidson and M. T. Bogert, *ibid.*, **57**, 151 (1935).

[5] H. Hock and Shon Lang, *Ber.*, **75B**, 300 (1942).

[6] (a) G. H. Sugimura and T. W. Reynolds, paper presented before the Division of Physical and Inorganic Chemistry of the New York Meeting of the XIIth International Congress of Pure and Applied Chemistry, Abstracts, 607 (1951); (b) T. W. Reynolds and G. H. Sugimura, National Advisory Committee for Aeronautics, Technical Note 2342 Cleveland (1951).

TABLE I

PROPERTIES OF 1-ALKYL-1,2,3,4-TETRAHYDRONAPHTHALENES

Alkyl substituent	B.p., °C. at 760 mm.	$n^{20}\text{D}$	d^{20}, g./ml.	Net heat of combustion,[a] kcal./mole at 25°	Kinematic viscosity,[b] centistokes				Analyses, %			
					32°F.	100°F.	140°F.	210°F.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
(None)[c]	207.41	1.5415	0.96935	1275	3.59	1.66	1.20	(0.79)[d]	90.85	90.80	9.15	9.16
1-Methyl	220.54	1.5353	.95825	1425	5.08	2.05	1.42	.88	90.35	90.39	9.65	9.70
1-Ethyl	239.46	1.5318	.95285	1570	6.18	2.25	1.54	.93	89.93	89.90	10.06	10.10
1-Butyl	273.00	1.5218	.93418	1860	12.54	3.48	2.20	1.22	89.29	89.18	10.71	10.69
1-Pentyl	289.49	1.5178	.92705	2010	16.91	4.30	2.59	1.39	89.04	88.99	10.96	11.02

[a] A.S.T.M. procedure D240-39. [b] Determined in viscosimeters calibrated with N.B.S. Standard viscosity samples and using A.S.T.M. procedure D445-46T. [c] The only crystallizable compound in this series was tetralin (1,2,3,4-tetrahydronaphthalene): f.p. −35.82°; heat of fusion, 3.75 kcal./mole (calculated from data selected from Mair and Streiff, *J. Research Natl. Bur. Standards*, **27**, 343 (1941)); estimated purity, 99.9 mole %. [d] Extrapolated value, since flow rate in viscosimeter was higher than that called for in A.S.T.M. procedure D445-46T.

packed with 1/4-inch Berl saddles.[6] Heart fractions of distillate with constant refractive index were combined for further purification. The steps of the purification included treatment with ferrous ammonium sulfate to remove any traces of tetralin hydroperoxide which might have been present, washing, drying, percolation through activated silica gel, and final fractional distillation in a six-foot Podbielniak column. The fractions of the final distillation were combined on the basis of constancy of refractive index, density and freezing point. Physical properties were determined after a final passage of the hydrocarbon through activated silica gel.

Since it was not possible to crystallize any of the 1-alkyl-1,2,3,4-tetrahydronaphthalenes and thus obtain time–temperature curves for calculation of mole per cent. impurities, an estimate of the purity of the hydrocarbons reported herein could not be made according to the freezing point method of Glasgow, *et al.*[7]

The purity of these hydrocarbons may be assessed qualitatively from a consideration of several factors. The methods of synthesis and the nature of the purification techniques employed were comparable to those that have consistently afforded products of 99.5 mole per cent. purity or better both at this and at other laboratories. Furthermore, the quantities of reagents used permitted the isolation of a great number of small distillation fractions with constant physical properties, thus facilitating effective separation of the desired product from small amounts of impurities. On this basis it appears probable that the 1-alkyl-1,2,3,4-tetrahydronaphthalenes here described are of the order of 99 mole per cent. pure. The value of 99.9 mole per cent. for the purity of 1,2,3,4-tetrahydronaphthalene was determined by the method of Glasgow, *et al.*[7]

The physical properties of the five hydrocarbons are listed in Table I. The boiling points, refractive indices, densities, net heats of combustion, and kinematic viscosities at four selected temperatures were determined by procedures previously described.[8] Many of these values are being reported for the first time.

Experimental

Purification of 1,2,3,4-Tetrahydronaphthalene.—In a column 30 feet long, two inches in diameter, packed with 1/4-inch Berl saddles, 25 kg. of commercial tetralin (Fine Chemicals Division, E. I. du Pont Co.) was distilled. Four kilograms of the heart fractions of constant refractive index material was taken for further purification.

After treatment with an excess of a solution of ferrous ammonium sulfate, the hydrocarbon was washed well with water and dried over successive portions of dried magnesium sulfate. The material was then passed through several columns of activated silica gel and finally fractionally distilled in a six-foot Podbielniak column. Fractions of constant refractive index, density and freezing point were combined and again passed through silica gel.

1-Ethyl-2,3,4-trihydronaphthalene-1-ol and its Dehydration.—Two duplicate preparations were carried out simultaneously as follows: To 146 g. (6.0 g. atoms) of magnesium turnings covered with one liter of absolute ether were added a few drops of ethyl bromide. After the start of the reaction had been assured, a solution of 654 g. (6.0 moles) of ethyl bromide in 800 ml. of absolute ether was added dropwise with vigorous stirring over a period of approximately three hours, maintaining the reaction mixture at 20° during this time.

After the reaction mixture had been stirred for an additional hour, while maintaining the reaction temperature between 20 and 25°, 730 g. (5.0 moles) of 1-tetralone (Edcan Laboratories, $n^{20}\text{D}$ 1.5703) in 1000 ml. of absolute ether was added over a period of 1.5 hours, with stirring. Upon completion of the addition, the reaction temperature was raised to between 25 and 35° and maintained at that temperature for another 2.5 hours. The reaction mixture was allowed to stir at room temperature for an additional 16 hours.

Addition of an excess of a saturated aqueous ammonium chloride solution effected decomposition of the Grignard complex. The precipitate was separated and treated further with dilute hydrochloric acid. This treatment caused the formation of an organic phase which was separated and washed with a dilute alkaline solution. After drying with anhydrous potassium carbonate, the material was distilled at reduced pressure (b.p. 104 to 111° at 2 mm.). Some evidence of dehydration was noted. The distillate had a $n^{20}\text{D}$ range of 1.5527–1.5614.

The ether solution from the original decomposition was washed with a sodium carbonate solution and with water, and dried over anhydrous potassium carbonate. After removal of the solvent by distillation at atmospheric pressure, the residue was distilled at reduced pressure. The bulk of the distillate, $n^{20}\text{D}$ 1.5503–1.5512, was combined with the material reported above from the decomposition of the salts. Boiling range of this crude 1-ethyl-2,3,4-trihydronaphthalene-1-ol was 104 to 111° at 2 mm. pressure.

The combined product from this and the duplicate preparation was dehydrated, using 50 g. of anhydrous cupric sulfate as a catalyst. This dehydration was considerably facilitated by stirring the reaction mixture with a "Trubore" stirrer (Ace Glass Company) while maintaining a temperature of 150° at 30 mm. pressure. The majority of the water was collected in a trap cooled with a Dry Ice–acetone mixture. The product, presumably a mixture of 1-ethyl-

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(7) A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

(8) I. A. Goodman and P. H. Wise, THIS JOURNAL, **72**, 3076 (1950).

3,4-dihydronaphthalene and 1-ethylidine-2,3,4-trihydronaphthalene, was filtered from the catalyst and then rapidly distilled through a short column. Fractions with $n^{20}\text{D}$ 1.5730 to 1.5711 were combined (b.p. 72 to 76° at 1 mm. pressure). The yield of distillate from two preparations was 1082 g. (6.8 moles, 68% of theory, based on 1-tetralone). Treatment of individual fractions with activated silica gel had no significant effect on the refractive indices. The infrared spectrum of the combined sample indicated the absence of detectible amounts of any unreacted alcohol and of 1-ethylnaphthalene, a possible dehydrogenation product.

1-Ethyl-1,2,3,4-tetrahydronaphthalene.—The hydrogenation of 1082 g. (6.8 moles) of the olefinic product was carried out in a rocking autoclave of approximately 4.5-l. capacity at 200°, at an initial pressure of 3000 p.s.i. of hydrogen using approximately 10% by weight of barium-promoted copper chromite as catalyst. The hydrogenation was completed in about one hour. The product was filtered from the catalyst. Treatment of the catalyst with refluxing ethanol afforded substantial quantities of hydrocarbon that had been adsorbed on the catalyst.

The hydrocarbon was fractionally distilled at approximately 50 mm. of pressure. The fractions of the distillate within the refractive index range of 1.5313 to 1.5322 were combined (785 g.) and refractionated in a six-foot Podbielniak column at 20 mm. pressure with a reflux ratio of approximately 200 to 1.

For combination of fractions from the final distillation, uniformity of composition was determined by constancy of refractive indices and densities of individual fractions.

After passage through columns of activated silica gel, 540 g. (3.4 moles) of high purity 1-ethyl-1,2,3,4-tetrahydronaphthalene was obtained (yield 34% of theory, based on 1-tetralone).

Summary of Preparations of 1-Alkyl-1,2,3,4-tetrahydronaphthalenes.—The details of the syntheses of the other hydrocarbons characterized in this report are essentially analogous to those described for the typical case of the preparation of 1-ethyl-1,2,3,4-tetrahydronaphthalene. In each instance, the Grignard reagent obtained from six moles of the appropriate halide was treated with five moles of 1-tetralone. Because of a general tendency of the resulting carbinols to dehydrate even on simple distillation, these materials were not highly purified prior to the dehydration step. The olefin mixture was hydrogenated in the presence of approximately 10% by weight of a barium-promoted copper chromite catalyst. No solvents were added to the hydrogenation charges, except in the case of the preparation of 1-pentyl-1,2,3,4-tetrahydronaphthalene in which a charge of 1230 ml. of olefins was reduced in the presence of 270 ml. of water-free dioxane. Initial hydrogen pressures were between 1800 and 3000 p.s.i., reaction temperatures between 190 and 210°. The purification procedures were also essentially similar to those employed for 1-ethyl-1,2,3,4-tetrahydronaphthalene. The experimental details are summarized in Table II.

TABLE II

SUMMARY OF EXPERIMENTAL DETAILS FOR THE PREPARATION OF 1-ALKYL-1,2,3,4-TETRAHYDRONAPHTHALENES

Alkyl substituent	B.p. range, °C. at 1 mm.	$n^{20}\text{D}$ range	Wt. of olefin, g.	Wt. of product isolated, g.	Yield, g.	Over-all yield based on 1-tetralone, %
1-Methyl	65–75	1.5768–1.5752	1102	1028	625	43
1-Ethyl	72–76	1.5730–1.5711	1082	785	540	34
1-Butyl	63–120	1.5740–1.5522	860	725	574	24
1-Pentyl[a]	94–102	1.5548–1.5479	1183	1125	675	33

[a] It is recognized that the 1-bromopentane could have been contaminated with other isomers. The density and refractive index of the 1-bromopentane were d^{20} 1.2206 g./ml. and $n^{20}\text{D}$ 1.4450 as compared with d^{20}_4 1.2160[9] and $n^{20}\text{D}$ 1.4448[10] in the literature. Data from propyl and butyl derivatives of several homologous series[2,8,11] show that branched chain impurities in the final hydrocarbon would have boiling points sufficiently lower than the boiling point of the desired compound to be removed by distillation.

Repeated efforts to prepare 1-(2-propyl)-1,2,3,4-tetrahydronaphthalene by a similar procedure resulted in exceedingly small yields of the final product in a state of purity that was considered too poor to permit inclusion of the compound in the present report.

Acknowledgment.—The authors wish to thank the members of the analytical and physical constants groups of this Laboratory for their assistance.

[9] W. H. Heston, Jr., E. J. Hennelly and C. P. Smyth, THIS JOURNAL, **72**, 2071 (1950).

[10] L. M. Kushner, R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 1091 (1950).

[11] I. A. Goodman and P. H. Wise, National Advisory Committee for Aeronautics, Technical Note 2419, Cleveland (1951).

CLEVELAND, OHIO

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. XXVII. Addition Reactions of Substituted *p*-Quinonedibenzenesulfonimides

BY ROGER ADAMS AND THOMAS E. YOUNG[1]

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Hydrogen chloride, thiophenol and sodium benzenesulfinate add readily to 2-methoxy-*p*-quinonedibenzenesulfonimide to give in excellent yield the 2-methoxy diamides with the chlorine, phenylmercapto and benzenesulfone groups in the 5-position. The products whose structures were proved by unequivocal syntheses were all readily oxidized to the corresponding diimides. 2-Chloro-*p*-quinonedibenzenesulfonimide adds sodium benzenesulfinate to give two isomeric benzenesulfones, one of which was proved unequivocally to be the 2-chloro-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide. 2-Phenylmercapto-*p*-quinonedibenzenesulfonimide adds sodium benzenesulfinate to give a high yield of 2-phenylmercapto-x-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide which upon oxidation with peroxide yields a 2,x-bis-(benzenesulfonyl)-*p*-phenylenedibenzenesulfonamide identical with that formed from the addition of thiophenol to 2-phenylmercapto-*p*-quinonedibenzenesulfonimide followed by peroxide oxidation. The orientation was not proved but is probably 2,5. 2-Methyl-*p*-quinonedibenzenesulfonimide adds thiophenol and sodium benzenesulfinate to give presumably the 2-methyl-5-phenylmercapto- and 2-methyl-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamides, respectively. The former was converted to the latter by peroxide oxidation.

p-Benzoquinones bearing a single electron-donating substituent undergo conjugate addition reactions to give predominantly 2,5-disubstituted hydroquinone derivatives. Methoxy-*p*-quinone, for example, undergoes the Thiele–Winter reaction to produce a 98% yield of 2-methoxy-1,4,5-triacetoxybenzene.[2] Toluquinone similarly gives good yields of 2-methyl-1,4,5-triacetoxybenzene,[3] and adds hydrogen chloride to produce chiefly 5-chlorotoluhy-

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[1] From portions of a thesis submitted by Thomas E. Young (Sept., 1952) to the Graduate College of the University of Illinois, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; Standard Oil Company of California Research Fellow, 1950–1952.

[2] H. G. H. Erdtman, *Proc. Roy. Soc.* (*London*), **A143**, 177 (1934).

[3] J. Thiele and E. Winter, *Ann.*, **311**, 349 (1900).