was measured using a Coleman Junior spectrophotometer set at 500 μ.

Since tube IV was essentially colorless, its transmission was set to read 100%. On this basis it was found that readings of per cent. transmission for the other tubes were I, 2%; II, 2%; and III, 8%. Without describing in detail the difficulties involved in the spectrophotometric determination, it is sufficient to say that the visible absorption spectra curves of the various ions are not well suited for a determination of this sort and the observed results have no quantitative meaning. Qualitatively it is definite that perinaphthene is less acidic than cyclopentadiene and more acidic than triphenylmethane. Possibly it is more acidic than fluorene. Additional evidence for this was the visual observation that fluorene discharged the color of sodium triphenylmethyl and on addition of perinaphthene this solution became blood-red.

A study of the reaction of perinaphthenyllithium with carbon dioxide was made in an attempt to apply the procedure of Conant and Wheland[19] for determining acidity. However, the product of this reaction was a deep green solid, m. p. 195–197°, with dec. This material dissolved readily in base, whereupon the green solution became brick-red and acidification then yielded a high-melting red solid. This behavior does not fit a simple carboxylic acid derivative, and the material is being investigated further.

Under the usual conditions of the Zerewitinoff and lithium aluminum hydride procedures for determining active hydrogen,[23] perinaphthene showed no active hydrogen. That this was due to a slow rate of attaining equilibria was shown by the fact that, on heating a mixture of perinaphthene and lithium aluminum hydride in ether, slow evolution of hydrogen occurred and the solution became orange, indicating the formation of the perinaphthenyl ion.

(h) Exchange Reaction with Triphenylmethyl.—A solution of triphenylmethyl, prepared under nitrogen by the reaction of excess zinc with 2.8 g. of triphenylmethyl chloride, was added with rigid exclusion of air to 0.53 g. of perinaphthene. The color of the reaction mixture slowly changed from yellow-orange to a fluorescent olive green. To complete the reaction the mixture was heated at 50° for three hours. The flask was then opened and the contents were poured into a beaker. Precipitation of a black solid began immediately and this was hastened by bubbling oxygen through the solution. The dark solid was collected, but it had a very high m. p. (above 330°) and was too insoluble in organic solvents to be purified. The mother liquor was purified by chromatography using activated alumina, and there was obtained 0.50 g. (63%, based on perinaphthene) of triphenylmethane, m. p. 93–94°.[24]

Summary

A practical synthesis of perinaphthene has been developed. The concept that the symmetry of the perinaphthenyl nucleus makes possible a high degree of resonance stabilization has been used to explain certain results in this series including the reaction of perinaphthenone with lithium aluminum hydride. It has been found that perinaphthene resembles fluorene, indene, and cyclopentadiene in many respects.

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[23] Krynitsky, Johnson and Carhart, THIS JOURNAL, **70**, 486 (1948).

[24] Kekule and Franchimont (*Ber.*, **5**, 906 (1872)) give the m. p. as 92.5°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

Alkyl Tetrahydronaphthalenes. II

BY ROBERT T. HART, W. J. GEORGITIS AND R. H. WELLS

In a previous paper,[1] a start was made toward the synthesis of a series of pure hydrocarbons and the correlation of their physical constants with molecular structure. In the present article, the alkyl tetralin series is extended by twenty new[2] members comprising four different types; monoalkyl, dialky, ω-cyclohexylalkyl and phenylalkyl. The method of synthesis is identical with that employed previously.

In the calculation of the theoretical values for the molar refractions ($M_{\text{D calcd.}}$), the values of the atomic refractions used were those of Swietoslawski.[3] The observed molar refractions ($M_{\text{D obs.}}$) were calculated by the Lorentz–Lorenz equation for specific refraction, using the experimental values for density and refractive index. As can be seen from Table I, there exists a considerable exaltation of the observed molar refractions over those calculated on the basis of molecular structure. This effect is expressed as the "specific-exaltation," $E\Sigma = 100EM/m$,[4] where EM is the molar exaltation and m is the molecular weight.

It has been reported[5] that, in calculation of the observed molar refraction, the increment for the CH_2 group within a normal chain, in different series of liquid substances at 20°, differs from an average value of 4.63 for the D line only by a few hundredths of a cc. The average value of the CH_2 increment, determined experimentally here for the thirteen tetralins to which the statement is applicable, was found to be 4.63, thus demonstrating an excellent agreement.

In attempting to correlate the physical constants with molecular structure, a perusal of the data in Table I reveals many interesting relationships, both qualitative and quantitative. As expected, the boiling points of the 6-isohexyl and 6,7-diisohexyl tetralins are lower than those of the isomeric n-hexyltetralins. Also, the boiling point, density and refractive index data for the 6-benzyl and 6-β-phenethyltetralins reflect their aromatic character when contrasted to their cyclohexyl analogs.

In submitting the boiling point data to statis-

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[1] Hart and Robinson, THIS JOURNAL, **70**, 3731 (1948).

[2] Those denoted with letter [a], Table I, are reported in the literature as "structure uncertain."

[3] Swietoslawski, THIS JOURNAL, **42**, 1945 (1920).

[4] Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 442.

[5] Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p. 679.

TABLE I

TETRAHYDRONAPHTHALENE DERIVATIVES

Compound	Yield, %[b]	Empirical formula	B. p., °C. (5 mm.)	d^{20}_4	n^{20}_D	$\gamma_{D\,obs.}$	M_D Calcd.	M_D Obs.	EΣ	Analyses, %[c] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
						Monoalkyl							
6-*n*-Hexyl[a]	69	$C_{16}H_{24}$	154–155.4	0.9224	1.5177	0.328	70.4	71.0	0.3	88.8	89.0	11.2	11.0
6-Isohexyl[d]	64	$C_{16}H_{24}$	150.6–151.6	.9156	1.5150	.329	70.4	71.2	.4	88.8	89.1	11.2	11.1
6-*n*-Heptyl	67	$C_{17}H_{26}$	167–168.5	.9142	1.5138	.329	75.0	75.8	.3	88.6	88.8	11.4	11.2
6-*n*-Octyl[a]	58	$C_{18}H_{28}$	180–181.5	.9101	1.5110	.329	79.6	80.4	.3	88.4	88.3	11.6	11.4
6-*n*-Nonyl	60	$C_{19}H_{30}$	192–194	.9079	1.5093	.329	84.2	85.0	.3	88.3	88.6	11.7	11.6
						Dialkyl							
6-*n*-Hexyl-7-*n*-propyl	59	$C_{19}H_{30}$	176–177.6	.9137	1.5140	.329	84.2	85.2	.4	88.3	88.5	11.7	11.5
6-*n*-Heptyl-7-*n*-propyl	61	$C_{20}H_{32}$	188–189	.9105	1.5120	.329	88.8	89.8	.4	88.2	87.9	11.8	11.9
6-*n*-Octyl-7-*n*-propyl	56	$C_{21}H_{34}$	197–198	.9079	1.5100	.329	93.4	94.4	.3	88.0	87.8	12.0	11.8
6-*n*-Nonyl-7-*n*-propyl	57	$C_{22}H_{36}$	207–208.1	.9042	1.5072	.329	98.0	98.9	.3	87.9	87.9	12.1	12.1
6-*n*-Octyl-7-*n*-butyl	55	$C_{22}H_{36}$	207–209	.9077	1.5100	.329	98.0	99.0	.3	87.9	87.5	12.1	12.2
6-*n*-Heptyl-7-*n*-amyl	62	$C_{22}H_{36}$	205–207	.9077	1.5100	.329	98.0	99.0	.3	87.9	87.9	12.1	12.4
6,7-Di-*n*-hexyl[a]	59	$C_{22}H_{36}$	203–204	.9077	1.5090	.329	98.0	98.9	.3	87.9	87.7	12.1	11.9
6,7-Di-isohexyl[d]	55	$C_{22}H_{36}$	198.5–200	.9026	1.5065	.329	98.0	99.0	.3	87.9	87.9	12.1	12.3
						ω-Cyclohexylalkyl							
6-Cyclohexylmethyl	50	$C_{17}H_{24}$	170–171.3	.9796	1.5434	.322	72.9	73.5	.3	89.4	89.3	10.6	10.6
6-(β-Cyclohexyl)-ethyl	52	$C_{18}H_{26}$	180.5–182	.9707	1.5386	.323	77.5	78.3	.3	89.2	89.2	10.8	10.7
6-(γ-Cyclohexyl)-propyl	52	$C_{19}H_{28}$	194–195.4	.9580	1.5328	.324	82.1	83.0	.4	89.0	88.9	11.0	11.0
6-(δ-Cyclohexyl)-butyl	57	$C_{20}H_{30}$	206–207	.9521	1.5294	.324	86.7	87.7	.4	88.8	88.8	11.2	11.1
6-(ε-Cyclohexyl)-amyl	64	$C_{21}H_{32}$	217.6–218.2	.9486	1.5260	.324	91.3	92.0	.3	88.7	88.9	11.3	11.1
						Phenylalkyl							
6-Benzyl	37	$C_{17}H_{18}$	176–177.5	1.0372	1.5878	.324	71.7	72.1	.2	91.8	92.1	8.2	8.1
6-(β)Phenethyl	41	$C_{18}H_{20}$	186–187.5	1.0200	1.5790	.326	76.3	77.0	.3	91.5	91.4	8.5	8.8

[a] Reported in literature as "structure uncertain." [b] % yield: for monoalkyl tetralins, calculated on basis of tetralin as starting material; for dialkyl tetralins, calculated on basis of monoalkyl tetralin as starting material. [c] All analyses by Oakwold Laboratories, Alexandria, Va. [d] δ-Methylpentyl.

tical analysis, the data from the previous paper[1] were combined with the new data reported in this article in order to increase the number of members in each series and thus make the equations developed more broadly applicable. For this purpose, the compounds were divided into four groups, monoalkyl, symmetric dialkyl, asymmetric-dialkyl, and ω-cyclohexylalkyl tetralins (where all alkyl groups are normal), and the midpoints of the observed boiling point ranges were taken as the boiling point values for computation. The "least squares" method of fitting straight lines to the paired observations of boiling point (y) *versus* the number of carbon atoms (x) gave the equations

I, Monoalkyl $y = -60.67 + 13.36x$

II, Symmetrical dialkyl $y = -9.3 + 9.64x$

III, Asymmetric dialkyl $y = -19.52 + 10.35x$

IV, ω-Cyclohexylalkyl $y = -37.32 + 12.18x$

Since, in the previous paper, a linear equation was given for the relationship of boiling points *versus* number of carbon atoms for dialkyl tetralins, with no distinction made between symmetric and asymmetric distribution of side-chain carbon atoms, it is not surprising that the angle between II and III above is less than one degree, *i. e.*, II and III are essentially parallel.

There is statistical evidence on the basis of the new compounds reported here for believing that these relations, in particular no. I, may prove eventually, on the basis of more data, to be quadratic.

In the case of each equation the probability of obtaining by chance alone a value of F[6] as large or larger than the calculated values is less than 0.01. If these equations are considered in the form $y = a + bx$, then the standard error of the observations (Y) about the regression line and the standard errors of the given estimates of a and b are:

Equation	Standard error of a	Standard error of b	Standard error of Y
I	0.50	0.23	1.4
II	.62	.28	1.2
III	.36	.15	1.2
IV	.37	.34	0.8

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(6) F = regression mean square deviation/residual mean square deviation, H. A. Freeman, "Industrial Statistics," John Wiley and Sons, Inc., New York, N. Y., 1942.

The linear equations given here predict the midpoints of the boiling point ranges with a maximum error of 1.8%.

An interesting empirical relationship between the density and refractive index was developed and may be of some utility in enabling one to predict fairly accurately the density of an alkyl tetralin by measurement of the refractive index. The following least square linear equation between d^{20}_4 and n^{20}_D was found and proven to be significant

$$d^{20}_4 = -2.2483 + 2.0900n^{20}_{D_{obs.}}$$

Substitution of $n^{20}_{D_{obs.}}$ in this equation in the case of twenty-six alkyl tetralins of diverse types gave a maximum error in estimating the value of d^{20}_4 of less than one per cent. Exact determination of the density, would, of course, require experimental measurement.

Ultraviolet and infrared spectra of the compounds have been determined by the Bureau of Mines, Petroleum Experiment Station at Bartlesville, Oklahoma, and will be published in a catalog of such spectra issued by the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

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Summary

1. Twenty new 6-alkyl and 6,7-dialkyl tetralins have been synthesized and their physical constants determined.

2. Values for the specific refraction, the observed molar refraction, the theoretical molar refraction, and the specific exaltation have been calculated for these tetralins.

3. There is a well-defined linear relationship between the boiling points and the number of carbon atoms when the data are segregated into groups according to molecular types.

4. An empirical relationship between the density and refractive index of the alkyl tetralins is reported.

Orono, Maine Received July 7, 1949

[Contribution from the Laboratories of The University of Maryland]

The Reaction of Propylene Oxide with Methanol[1]

By Wilkins Reeve and Alexander Sadle[2]

The base catalyzed reaction of propylene oxide with methanol and ethanol has been shown recently by Petrov[3] and Chitwood and Freure[4] to give a product consisting almost entirely of one isomer, 1-alkoxypropanol-2. A mixture of 1-alkoxypropanol-2 and 2-alkoxypropanol-1 is obtained when an acid catalyst is employed.[3,4] A mixture of isomers is also obtained when no catalyst is used.[3,4] In the case of the ethoxypropanols, the evidence for the assigned structures is based on the cleavage of the ethoxy group by a small amount of sulfuric acid in acetic anhydride in one isomer (assigned the secondary ether structure) and not in the other.[4] The methoxypropanols were assigned their structures on the basis of oxidation products isolated in 10–15% yields.[3] Subsequent to our work, infrared absorption data have been reported.[5] The work of earlier investigators is reviewed by Petrov,[3] Chitwood and Freure,[4] and Kadesch.[6] No unequivocal syntheses of any of the isomeric alkoxypropanols have been reported, nor have crystalline derivatives of these compounds been prepared. Most of the published physical data on the products obtained by acid catalysis are questionable because of the difficulty of separating the mixture of isomers formed.

The object of the present work was to develop unequivocal syntheses for 2-methoxypropanol-1 and 1-methoxypropanol-2, to prepare suitable derivatives of these, and to compare these compounds with the products obtained by the reaction of methanol with propylene oxide.

2-Methoxypropanol-1 was prepared by the copper chromite catalyzed hydrogenolysis of ethyl α-methoxypropionate. The reduction of the ester proceeded normally and no by-products were detected. In view of its successful use in this case, this method holds promise of being generally applicable in the syntheses of pure 2-alkoxy-substituted primary alcohols. This reduction of α-alkoxy esters using the usual small amounts of catalyst does not appear to have been previously employed.

1-Methoxypropanol-2 was prepared by the reduction of methoxyacetone with hydrogen over Raney nickel catalyst. The methoxyacetone was prepared from methoxyacetonitrile and methylmagnesium bromide.

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[1] Presented before the Division of Organic Chemistry at the Chicago Meeting of the American Chemical Society, April, 1948.

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[3] Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **14**, 1038 (1944); **16**, 1206 (1946).

[4] Chitwood and Freure, This Journal, **68**, 680 (1946).

[5] Sexton and Britton, *ibid.*, **70**, 3606 (1948). This paper was submitted after our results had been presented at the 1948 Chicago meeting. No description is given of the isomers used.

[6] Kadesch, *ibid.*, **68**, 41 (1946).