Direct oxidation of IX with sodium dichromate in acetic acid gave a poor yield of neutral product, which appeared to be a mixture.

8-Methylperinaphthanol-7 (X).—The preparation of 8-methylperinaphthanone-7 was carried out as described by Fieser and Novello.[13] The reduction of 8-methylperinaphthanone-7 was accomplished with lithium aluminum hydride by the general procedure given for the reduction of perinaphthanone-7.[2] From 25 g. of ketone there was obtained 23.4 g. (96%) of 8-methylperinaphthanol-7 as white needles m. p. 149–150°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.84; H, 7.07. Found: C, 85.10; H, 7.03.

The phenylurethan of 8-methylperinaphthanol-7 was obtained from alcohol as white needles, m. p. 147–149°.

Anal. Calcd. for $C_{21}H_{19}NO_2$: C, 79.49; H, 5.99. Found: C, 79.23; H, 5.93.

8-Methylperinaphthene (XI).—The dehydration of 8-methylperinaphthanol-7 was carried out as described for the preparation of IX. From 5.0 g. of alcohol there was obtained 4.0 g. (89%) of 8-methylperinaphthene as a white solid, m. p. 57–58°.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.46; H, 6.83.

The picrate of 8-methylperinaphthene was obtained from alcohol as brick-red needles, m. p. 127° dec.

Anal. Calcd. for $C_{20}H_{15}N_3O_7$: C, 58.71; H, 3.67. Found: C, 58.99; H, 3.75.

The trinitrobenzene derivative of 8-methylperinaphthene was obtained from alcohol as fine orange needles, m. p. 160° dec.

Anal. Calcd. for $C_{20}H_{15}N_3O_6$: C, 61.09; H, 3.85. Found: C, 60.79; H, 3.84.

Several of the first preparations of the T.N.B. derivative gave orange needles, m. p. 149–150° dec., and it is possible that this corresponds to the T.N.B. derivative obtained by Fieser and Novello[13] from the Clemmensen reduction of 8-methylperinaphthanone-7.

8-Methylperinaphthane. (a) **Hydrogenation of 8-Methylperinaphthene (XI).**—A solution of 1.2 g. of 8-methylperinaphthene in 60 ml. of methanol was shaken under 3 atm. of hydrogen pressure in the presence of 100 mg. of platinum oxide catalyst. When hydrogen ceased to be absorbed, the catalyst and solvent were removed. The residual oil was taken up in pentane and purified by chromatography over alumina. There was obtained 1.0 g. (83%) of 8-methylperinaphthane as a colorless oil.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.27; H, 7.73. Found: C, 92.31; H, 7.71.

The trinitrobenzene derivative of 8-methylperinaphthane was obtained from alcohol as fine yellow needles, m. p. 138–140°.

Anal. Calcd. for $C_{20}H_{17}N_3O_6$: C, 60.75; H, 4.34. Found: C, 61.26; H, 4.24.

The yield of T.N.B. derivative was essentially quantitative and no other product could be isolated.

(b) **Hydrogenolysis of 8-Methylperinaphthanol-7.**—This hydrogenolysis was carried out as previously described for the hydrogenolysis of 1-methylperinaphthanol-7. From 3.00 g. of 8-methylperinaphthanol-7 there was obtained 2.38 g. (83%) of 8-methylperinaphthane as a colorless oil.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.27; H, 7.73. Found: C, 92.41; H, 7.75.

The trinitrobenzene derivative was obtained from alcohol as fine yellow needles, m. p. 138–140°. A mixture of the T.N.B. derivatives from (a) and (b) showed no depression of melting point.

The infrared curves of 8-methylperinaphthane prepared from (a) and (b) are shown in Fig. 2.

Summary

Dehydration of four different methylperinaphthanols having the methyl group at the 1-, 3-, 7- and 9-positions, respectively, gave the same hydrocarbon, 1-(or 6)-methylperinaphthene. The same hydrocarbon was also obtained by alkylation of perinaphthene with methyl iodide and by the reaction of perinaphthenone with methylmagnesium iodide.

Dehydration of 8-methylperinaphthanol-7 gave 8-methylperinaphthene.

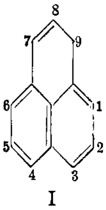
ROCHESTER, NEW YORK RECEIVED JULY 5, 1949

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

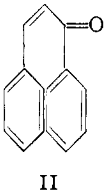
An Investigation of the Preparation and Some Properties of Perinaphthene[1]

BY V. BOEKELHEIDE AND CLIFFORD E. LARRABEE[2a,b]

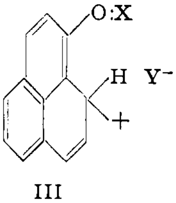
Perinaphthene (I) is a hydrocarbon of some interest because of its highly symmetrical structure. Because of the difficulty of preparing perinaphthene or its simple derivatives, most investigations in this series have been concerned with the oxygenated derivatives. These derivatives have shown a number of unusual properties and it would seem that a plausible explanation for this behavior is that the symmetry of the perinaphthenyl ion or radical makes possible a considerable amount of resonance stabilization of these entities. For example, perinaphthenone (II) dissolves in aqueous acid to give an orange solution[1,3] and also forms stable complexes with many reagents.[4,5] This behavior would be ex-



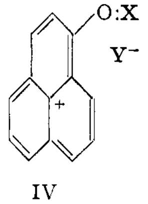
I



II



III



IV

---

[1] The nomenclature used is that suggested by Fieser and Hershberg (THIS JOURNAL, **60**, 1658 (1938)) and the numbering used for perinaphthene and its alkyl derivatives is illustrated in formula I.

[2] (a) Beaunit Mills Fellow, 1948–1949; (b) present address: General Aniline and Film Corp., Easton, Pennsylvania.

[3] See Cook and Hewett, *J. Chem. Soc.*, 368 (1934); Bamberger and Philip, *Ann.*, **240**, 178 (1887); and Vollman, Becker, Corell, and Streek, *ibid.*, **531**, 80 (1937).

[4] Zilberman and Barkov, *J. Gen. Chem.*, **7**, 1733 (1937); *C.A.* **32**, 538 (1938).

[5] Similar complexes are probably involved in the brominations reported by Lukin, *Bull. acad. sci. U. S. S. R., Classe sci. Chim.*, **1941**, 565, 695; *C. A.*, **37**, 2734 (1943).

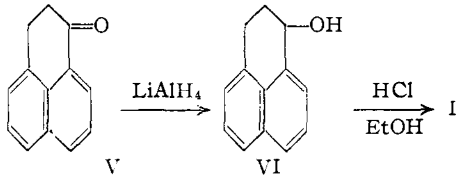
pected if structures of the carbonium ion type illustrated by III and IV made important contributions to the resonance hybrid.

The results of Koelsch and Anthes,[6] on the reduction of 9-phenylperinaphthenone, the anomalous Grignard additions of perinaphthenone[6,7] and its derivatives[8,9] and the results of Fieser and Gates on the Grignard reaction with perinaphthanone-7[10] may be interpreted in a similar manner based on the symmetry of the perinaphthenyl nucleus.

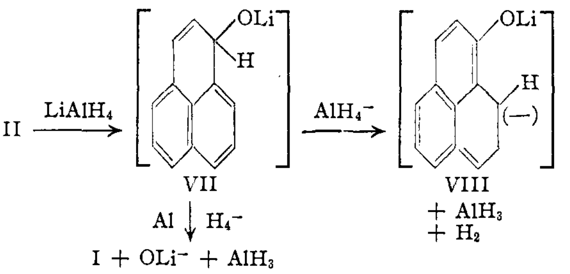
However, the effects of resonance stabilization in this series should be most easily discernible in perinaphthene itself or its simple alkyl derivatives. A study of the preparation of perinaphthene has therefore been made and it is the purpose of this paper to describe a practical synthesis of perinaphthene as well as to describe some of its properties.

Although a number of attempts have been made to prepare perinaphthene[7,11,12] its synthesis was only recently accomplished by Lock and Gergely, who reduced perinaphthenone by the Wolff–Kishner procedure.[13] This method was reported by Lock and Gergely to be useful only for preparing very small amounts of perinaphthene and, when our attempts to utilize their synthesis on a practical scale failed, other methods for preparing perinaphthene were investigated. It was found that perinaphthene could be conveniently prepared on a practical scale by the dehydration of perinaphthanol-7 using alcoholic hydrogen chloride as catalyst. Although other methods of dehydrating perinaphthanol-7 have been tried without success,[1,12] this procedure gave perinaphthene in consistent yields of 65 to 85%.

Perinaphthanol-7 (VI) has been previously prepared by the catalytic reduction of perinaphthenone using a two-year old lot of Raney nickel catalyst.[12] Unless the catalyst is properly deactivated, considerable quantities of phenolic material result and it proved more satisfactory to prepare perinaphthanol-7 by the lithium aluminum hydride reduction of the readily available perinaphthanone (V).[10] The preparation of perinaphthene is summarized below:



Another method of preparing perinaphthene was discovered inadvertently when the lithium aluminum hydride reduction of perinaphthenone was attempted in the hope of preparing perinaphthenol. This work was done prior to Hochstein's publication[14] on the same reaction and our results are somewhat different from those which he reported. The reaction proceeded with evolution of hydrogen and from the reaction mixture there was isolated perinaphthanone-7 (65% yield), perinaphthene (14%), and phenolic material (12%). These products are similar to those obtained in the Grignard reaction with perinaphthenone[15] and an explanation for the course of the reaction may be postulated as



The initial product, VII, may undergo further reaction to give either perinaphthene (I) or a second intermediate, VIII. It would be expected that on hydrolysis VIII would be converted to perinaphthanone-7, a phenol, or perinaphthenol, depending on the position on the perinaphthenyl nucleus taken by the incoming hydrogen. Addition of the hydrogen at the 7-position would give the enolic form of perinaphthanone-7, addition at the 9-position would yield perinaphthenol, and addition at any of the other possible positions would yield a phenol. Postulation of VIII as an intermediate is reasonable in view of the results of Trevoy and Brown[16] on the reaction of fluorene with lithium aluminum hydride and our own results on the reaction of perinaphthene with lithium aluminum hydride.

A preliminary investigation of the properties of perinaphthene has given the following results. Perinaphthene is unstable in contact with air, discoloring in a matter of hours and becoming completely black within a few days. Although it can be stored indefinitely in a sealed vial under nitrogen, it was found much more convenient to prepare samples of perinaphthene as needed just before using. Perinaphthanol-7 is fairly stable and can be stored. The ultraviolet absorption spectrum of perinaphthene is given in Fig. 1.

The observations of Lock and Gergely[13] that perinaphthene is reduced catalytically to perinaphthane and can be air-oxidized to perinaphthenone were confirmed. When the oxidation of perinaphthene was tried using sodium dichromate, perinaphthenone was obtained in 83% yield.

Perinaphthene showed many similarities to indene, fluorene and cyclopentadiene. It gave a

---

[6] Koelsch and Anthes, *J. Org. Chem.*, **6**, 558 (1941).

[7] Craig, Jacobs and Lavin, *J. Biol. Chem.*, **139**, 277 (1941).

[8] Koelsch and Rosenwald, *J. Org. Chem.*, **3**, 462 (1938).

[9] Koelsch and Rosenwald, THIS JOURNAL, **59**, 2166 (1937).

[10] Fieser and Gates, *ibid.*, **62**, 2335 (1940).

[11] von Braun and Reutter, *Ber.*, **59**, 1922 (1926).

[12] Fieser and Newton, THIS JOURNAL, **64**, 917 (1942).

[13] Lock and Gergely, *Ber.*, **77**, 461 (1944).

[14] Hochstein, THIS JOURNAL, **71**, 305 (1949).

[15] See the accompanying paper, *ibid.*, **72**, 1240 (1950).

[16] Trevoy and Brown, *ibid.*, **71**, 1675 (1949).

deep red color that quickly changed to green in the Vanscheidt color test,[17] and it condensed with benzaldehyde in the presence of base to form a brick-red product. Perinaphthene formed a blood-red solution on treatment with an ethereal solution of phenyllithium and, when this solution was treated with an excess of methyl iodide, alkylation occurred. Thus, the presence of a replaceable hydrogen atom was established. It was of interest that the alkylation product was identical with the methylperinaphthene previously prepared by Fieser and Newton[12] and by Craig, Jacobs and Lavin.[7,15]

At present no clear decision can be made in regard to the stability of perinaphthenyl ions and radicals. Attempts to prepare 9-bromoperinaphthene, which would be a key compound in determining the stability of carbonium ions and in preparing the perinaphthenyl radical, have been unsuccessful. Bromination of perinaphthene in the cold readily gave the corresponding dibromo compound, but attempts to dehydrobrominate the dibromo compound yielded deeply-colored green-blue solutions from which it has not been possible to isolate and establish a monobromo product. Bromination with N-bromosuccinimide or bromination at room temperature and above likewise yielded highly colored solutions from which no clean product was isolated.

It was possible to carry out two experiments having some bearing on resonance stabilization in this series. On the basis of color determinations in exchange reactions it was found that perinaphthene was definitely more acidic than triphenylmethane and less acidic than cyclopentadiene. Because of difficulties involved in this determination it was not possible to accurately relate the acidity of perinaphthene to that of fluorene and indene, two hydrocarbons which are also intermediate in acidity between triphenylmethane and cyclopentadiene.[18] It was not possible to use the carbonation procedure of Conant and Wheland for determining acidity[19] because perinaphthene showed an anomalous behavior in the carbonation reaction.

In another experiment perinaphthene was added to a solution of triphenylmethyl. The color of the solution gradually changed from yellow-orange to a fluorescent olive green, and from the reaction mixture there was isolated a good yield of triphenylmethane. Perinaphthene apparently served as a hydrogen donor molecule for the triphenylmethyl radical. A further study of perinaphthenyl ions and radicals is planned.

Experimental[20]

Preparation of Perinaphthene: (a) By Dehydration of Perinaphthanol-7.—Perinaphthanol-7 was prepared by the lithium aluminum hydride reduction of perinaphthanone-7.[10] Perinaphthanone-7 (60 g., 0.33 moles) in 400 ml. of dry ether was slowly added to 200 ml. of a 0.5 M ethereal solution of lithium aluminum hydride. After the addition was complete, the reaction mixture was stirred for ten minutes and then decomposed with water followed by addition of sufficient dilute hydrochloric acid to dissolve the precipitated salts. The organic layer was separated, dried, and the ether was removed. The residual oil, on treatment with pentane, crystallized yielding 56 g. (92%) of perinaphthanol-7, m. p. 85°. Although the material, thus obtained, is not completely pure, it is sufficiently good for use in the next step.

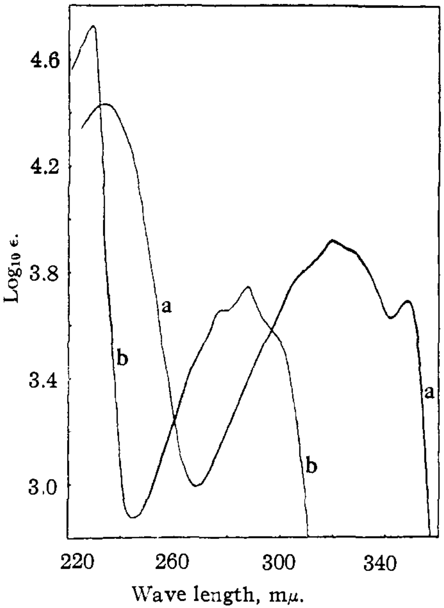


Fig. 1.—Ultraviolet absorption spectra of perinaphthene (a) and perinaphthane (b) in ethanol, principal maxima and log ε values: (a) 348 mμ (3.7), 320 mμ (3.9), and 234 mμ (4.4); (b) 289 mμ (3.7) and 228 mμ (4.7).

The dehydration of perinaphthanol-7 was done many times and the yields ranged from 65 to 85%. The following run is typical. To a solution of 2.0 g. of perinaphthanol-7 in 10 ml. of absolute alcohol there was added 10 ml. of a solution of absolute alcohol saturated with hydrogen chloride. The resulting solution was boiled under reflux for fifteen minutes and during the heating period the color of the solution changed from orange to a deep blue. When the solution had cooled, it was poured into 100 ml. of water and the aqueous solution was extracted with pentane. The pentane solution was dried and then concentrated to a volume of 30 ml. When this solution was chromatographed using activated alumina,[21] there was obtained from the colorless pentane eluate 1.6 g. (85%) of perinaphthene as colorless plates, m. p. 85–86° (lit.,[13] m. p. 85°).

The picrate of perinaphthene formed readily and, after recrystallization from ethanol, was obtained as brick-red needles, m. p. 205–207°, with dec.[22]

Anal. Calcd. for $C_{19}H_{13}N_3O_7$: C, 57.69; H, 3.32. Found: C, 57.36; H, 3.16.

The trinitrobenzene derivative of perinaphthene was

---

[17] Vanscheidt, *J. Gen. Chem., U. S. S. R.*, **4**, 875 (1934).

[18] Wheland, "The Theory of Resonance," J. Wiley and Sons, New York, N. Y., 1944, p. 173.

[19] Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

[20] Analyses by Mrs. G. Sauvage; all melting points are uncorrected.

[21] The activated alumina used throughout this investigation was prepared by heating aluminum hydroxide (Baker and Adamson) of 80–200 mesh at red heat until bubbling no longer occurred on stirring. This proved to be superior to all other samples of activated alumina tried including several from commercial sources.

[22] Lock and Gergely (ref. 13) report the picrate as m. p. 110°, with dec.

obtained, after crystallization from alcohol as fine orange needles, m. p. 159°, with dec.

Anal. Calcd. for $C_{19}H_{13}N_3O_6$: C, 60.19; H, 3.45. Found: C, 60.19; H, 3.35.

(b) **By Reduction of Perinaphthenone with Lithium Aluminum Hydride.**—A gas-tight system was prepared consisting of a reaction flask connected to a Soxhlet apparatus which in turn was connected to a gas-collecting device. Five grams of perinaphthenone was placed in the Soxhlet, an excess of a 0.5 *M* ethereal solution of lithium aluminum hydride was placed in the reaction flask, the air was displaced by nitrogen, and the system was closed. The solution in the reaction flask was boiled gently until all of the perinaphthenone had been introduced into the reaction mixture. Gas evolution corresponded to approximately one molar equivalent and its behavior on combustion indicated it to be hydrogen. The reaction mixture was hydrolyzed with sufficient aqueous hydrochloric acid to give a clear solution and the ether layer was separated.

After it had been washed with a 5% aqueous sodium hydroxide solution, the ether layer was dried and then chromatographed over alumina. The first fraction of eluate contained 0.7 g. (14%) of white plates, m. p. 85°, which was shown to be perinaphthene by formation of the picrate, m. p. 205–207°, with dec. The second fraction of 0.2 g. of a yellow oil was not identified. The third fraction contained 3.3 g. (65%) of light crystals, m. p. 85° which was shown by formation of the oxime, m. p. 125°, to be perinaphthanone.[10] By acidification of the basic extract an additional 0.6 g. (12%) of a red oil resulted, which appeared to be phenolic since it gave a deep red ferric chloride test.

Hochstein[14] made no mention in his publication of any other product than perinaphthene nor did he indicate how he distinguished between perinaphthene and perinaphthanone.

Reactions of Perinaphthene: (a) General Properties.—Perinaphthene, when freshly prepared, formed beautiful white plates but on exposure to air for several hours the crystals became tinged with green and within a day or two they became completely black. Samples stored in a sealed vial under nitrogen appeared to be quite stable. When a pinch of perinaphthene was added to an alcoholic solution of potassium hydroxide, the solution turned red and then quickly became green indicating a positive Vanscheidt color reaction.[17] Treatment of perinaphthene with either phenyl azide or an ethereal solution of diazomethane gave no reaction.

(b) **Reduction.**—Lock and Gergely have reported the reduction of perinaphthene to perinaphthane.[13] This reduction was found to proceed in a quantitative fashion with platinum oxide as catalyst and methanol as solvent. The identity of the perinaphthane, m. p. 65°, was established by preparation of the picrate, m. p. 148–150°.

(c) **Oxidation.**—Air oxidation of perinaphthene to perinaphthenone was confirmed in the following way. The dark tarry mass, produced by allowing perinaphthene to stand in the presence of air for several days, was taken up in benzene and passed over a column of aluminum. From the eluate there was obtained a sample of perinaphthenone in poor yield which, after sublimation, melted at 148°. A mixture of this with an authentic sample of perinaphthenone showed no depression of melting point.

Although air oxidation of perinaphthene to perinaphthenone was very poor, oxidation of perinaphthene with sodium dichromate solution occurred in good yield. A solution of 1.0 g. of perinaphthene in 5 ml. of glacial acetic acid was added to a mixture of 7 g. of sodium dichromate in 25 ml. of acetic acid. A considerable amount of heat was evolved during the addition and, after this initial reaction was over, the mixture was heated on the steam-bath for two hours. The mixture was then poured into water and the solid that separated was collected. There was obtained 0.9 g. (83%) of perinaphthenone, m. p. 153–155°, which was identified as before.

(d) **Condensation with Benzaldehyde.**—A mixture of 300 mg. of perinaphthene, 30 ml. of ether, 10 ml. of alcohol, 0.3 g. of benzaldehyde, and 0.5 ml. of a 10% aqueous sodium hydroxide was sealed under a nitrogen atmosphere and allowed to stand at room temperature for one week. Sufficient benzene was then added to redissolve the red-brown solid, which had precipitated; the solution was washed with water; and the ether was removed. The volume was increased to 50 ml. by addition of hexane and the solution was passed over alumina. From the first fraction there was obtained 150 mg. (33%) of an amorphous orange solid, m. p. 190°. Further attempts at purification did not yield a crystalline product.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 93.62; H, 6.05.

From the second fraction there was obtained a highly insoluble orange solid, m. p. about 330, which was not further characterized.

(e) **Alkylation with Methyl Iodide.**—To a solution of 1.85 g. of perinaphthene in 25 ml. of absolute ether there was added 15 ml. of an ethereal 1.33 *M* phenyllithium solution. To the blood-red solution, thus produced, there was added dropwise a solution of 5 g. of methyl iodide in 25 ml. of ether. This caused the color of the solution to change to a green-blue. The solution was washed with water, dried, and the ether was removed. The residual oil was taken up in pentane and purified by chromatography using activated alumina. There was obtained 1.65 g. (82%) of white crystals, m. p. 60–64°.

Prior to subjecting the residual oil to chromatography, a portion of it was converted to the trinitrobenzene derivative, which was obtained as orange needles, m. p. 135°. These properties show the product to be 1(or 6)-methylperinaphthene.[15] The fact that the trinitrobenzene derivative was formed prior to chromatography, indicates that the isomerization which has occurred in the formation of the 1(or 6)-methylperinaphthene, did not result from passing the compound over alumina. It was also shown that, if the blood-red solution produced by addition of phenyllithium to perinaphthene were treated with water, perinaphthene would be recovered quantitatively.

(f) **Bromination.**—A solution of 0.70 g. of bromine in 10 ml. of carbon tetrachloride was added dropwise to a solution of 0.76 g. of perinaphthene in 25 ml. of carbon tetrachloride. The reaction flask was rotated in a cooling bath of dry ice-acetone during the addition. The solution was decanted from a gummy orange precipitate, and pentane was added. When the solution was cooled, white crystals separated which were removed and recrystallized from a mixture of carbon tetrachloride and pentane. There was obtained 0.65 g. (45%) of 7,8-dibromoperinaphthane, m. p. 102–104°.

Anal. Calcd. for $C_{13}H_{10}Br_2$: C, 47.89; H, 3.09. Found: C, 48.41; H, 3.22.

The crystals lost hydrogen bromide on standing and became highly colored in a short period of time. The poor analysis is attributed to loss of hydrogen bromide. Attempts to dehydrobrominate the dibromo compound were made by heating it in glacial acetic acid and also in pyridine. In both cases deep green-blue solutions were formed but no clean product could be isolated. Likewise, when a solution of perinaphthene in carbon tetrachloride was treated with N-bromosuccinimide, a fairly vigorous reaction occurred during which hydrogen bromide was evolved and the solution became a deep blue-green. No useful product was isolated.

(g) **Acidity Determinations.**—For the determination of acidity of perinaphthene four sample tubes were prepared containing the following solutions under nitrogen. Tube I contained 10 ml. of a 0.05 *M* ethereal solution of perinaphthene, 10 ml. of a 0.05 *M* ethereal solution of sodium triphenylmethyl, and 10 ml. of absolute ether. Tube II was the same as tube I except that 10 ml. of a 0.05 *M* ethereal solution of fluorene was substituted for the 10 ml. of absolute ether. Similarly for tube III the absolute ether was substituted by 10 ml. of a 0.05 *M* ethereal solution of indene, and for tube IV the absolute ether was substituted by 10 ml. of a 0.05 *M* ethereal solution of cyclopentadiene. The intensity of color in each of the tubes 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.

ROCHESTER, NEW YORK RECEIVED JULY 5, 1949

---

(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°.

[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 ($MD_{\text{calcd.}}$), the values of the atomic refractions used were those of Swietoslawski.[3] The observed molar refractions ($MD_{\text{obs.}}$) 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-

---

(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.