prepared and converted into methyl α-(N-phenacetyl) - benzylamino - β,β - dimethoxypropionate. Some of the reactions of these substances and of the intermediates from which they were prepared have been studied.

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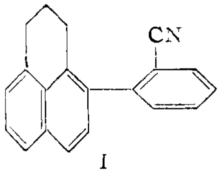
[Contribution from the Department of Chemistry, University of Rochester]

A Study of Isomerization in the Methylperinaphthene Series

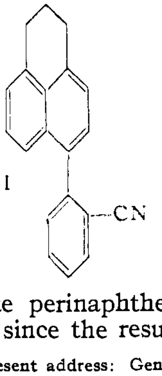
By V. Boekelheide and Clifford E. Larrabee[1]

Perinaphthene and its derivatives exhibit some unusual properties and the explanation has been advanced that, because of the symmetry of the molecule, the corresponding ions and radicals have a relatively high degree of stabilization due to resonance.[2] One implication of the resonance concept is that all of the monosubstituted perinaphthenes having the same substituent variously placed at the 1-, 3-, 4-, 6-, 7- or 9- positions should, on conversion to the corresponding anion followed by acidification, yield the same product or the same mixture of products. For the purpose of testing this idea a study of the preparation and isomerization of some methylperinaphthenes has been made.

That symmetry might be an important factor in influencing the behavior of perinaphthene and its derivatives was first suggested by Klyne and Robinson,[3] who proposed that perinaphthene derivatives, when prepared, would be found to be tautomeric. Although they were unsuccessful in preparing 1-methylperinaphthene, they thought that it should exist as a mixture of six forms corresponding to the six positions possible for the "extra" hydrogen on the nucleus. Evidence that perinaphthene derivatives may be readily isomerized was first obtained by Fieser and Gates,[4] who found that the reaction product of *o*-chlorophenylmagnesium bromide and perinaphthanone, when subjected to dehydration, hydrogenation and treatment with cyanide, gave two products, I and II. Presumably the intermediate perinaphthene derivative isomerized to a mixture.



I

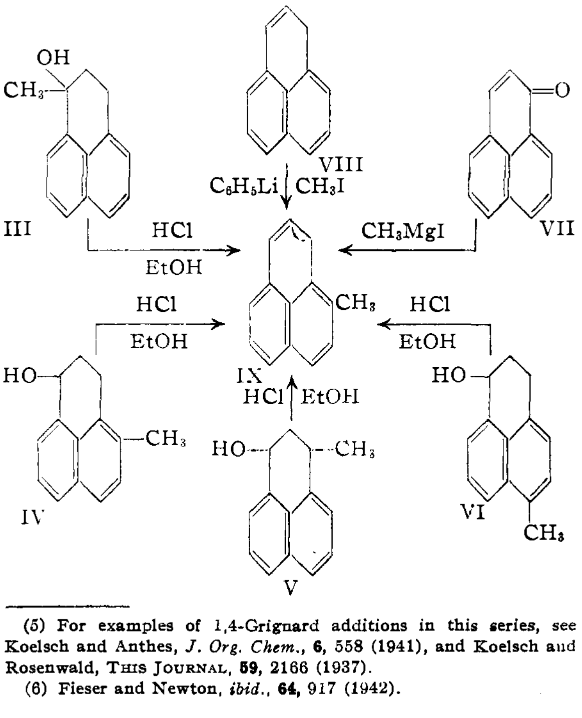


II

However, since the intermediate perinaphthene derivative was not isolated and since the results can also be interpreted on the basis that the Grignard addition occurred in both a 1,4- and 1,6- fashion,[5] isomerization was not established.

For the investigation of isomerization in the methylperinaphthene series, it seemed desirable to try to prepare several different methylperinaphthenes in order to determine whether interconversion would occur. Of the methods available for preparing perinaphthene derivatives, the most feasible appeared to be dehydration of the appropriate carbinol. This method was used by Fieser and Newton[6] for converting the tertiary alcohol, 7-methylperinaphthanol-7, to a methylperinaphthene, and it has been used recently for preparing perinaphthene in good yield.[2] Therefore the various alcohols shown by formulas III, IV, V and VI were prepared for use in the dehydration step.

The preparation of III and IV has been previously described.[3,6] In the preparation of V, 9-methylperinaphthanone-7 was obtained from α-naphthyl methyl ketone by the successive steps of Reformatsky addition of ethyl bromoacetate, dehydration, hydrolysis, hydrogenation and cy-



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[2] See the accompanying paper, This Journal, **72**, 1245 (1950).

[3] Klyne and Robinson, *J. Chem. Soc.*, 1991 (1938).

[4] Fieser and Gates, This Journal, **62**, 2335 (1940).

[5] For examples of 1,4-Grignard additions in this series, see Koelsch and Anthes, *J. Org. Chem.*, **6**, 558 (1941), and Koelsch and Rosenwald, This Journal, **59**, 2166 (1937).

[6] Fieser and Newton, *ibid.*, **64**, 917 (1942).

clization by means of hydrogen fluoride. Reduction of 9-methylperinaphthanone-7 to V was accomplished in excellent yield using lithium aluminum hydride. For the preparation of VI, α-methylnaphthalene was chloromethylated to give 1-methyl-4-chloromethylnaphthalene, which was then used to alkylate diethyl malonate. Hydrolysis and decarboxylation gave the corresponding propionic acid, which was cyclized by means of hydrogen fluoride to give 3-methylperinaphthanone-7. VI was obtained from the ketone by the use of lithium aluminum hydride as before. All four of the alcohols, thus prepared, were obtained in good over-all yield.

When dehydration of the four alcohols was tried, it was found that the same methylperinaphthene was formed from each. This hydrocarbon, m. p. 63–65°, was obtained in good yield in every case and is identical with the hydrocarbon previously reported by Fieser and Newton to be formed by dehydration of 7-methylperinaphthanol-7 (III).[6] It is obvious that for at least three of the alcohols dehydration must have been accompanied by isomerization. In an attempt to determine the nature of the isomerization the structure of the hydrocarbon, thus produced, was investigated as follows.

Catalytic hydrogenation of the hydrocarbon gave a dihydro derivative which was an oil whose trinitrobenzene (T.N.B.) derivative was yellow and melted at 147–149° without decomposition. Of the structures possible for the dihydro compound the only one which has previously been prepared is 1-methylperinaphthane. Buu-Hoï and Cagniant[7] state that the Clemmensen reduction of 1-methylperinaphthanone-7 gave 1-methylperinaphthane, whose T. N. B. derivative was yellow and melted at 134–135°, dec. When the Clemmensen reduction of 9-methylperinaphthanone-7 was carried out, an impure oil resulted whose T. N. B. derivative also melted at 134–135° dec., and which appeared to be the same as the T. N. B. derivative of the hydrocarbon resulting from the dehydrations of III, IV, V and VI.

The possibility that the Clemmensen reduction had yielded a mixture containing some of the unknown hydrocarbon was further strengthened when it was found that Wolff–Kishner reduction of 1-methylperinaphthanone-7 gave an oil, whose T.N.B. derivative was yellow and melted at 147–149° without decomposition. Also, high pressure hydrogenolysis of 1-methylperinaphthanol-7 (IV) gave an oil, whose properties were in agreement with those of the oil from the Wolff–Kishner reduction. A comparison of 1-methylperinaphthane, produced by the hydrogenolysis of IV, and the dihydro derivative of the unknown hydrocarbon showed them to be identical. The infrared absorption curves of the two samples are given in Fig. 1. In addition the ultraviolet absorption curves were alike and mixtures of the two T.N.B. derivatives showed no depression of melting point.

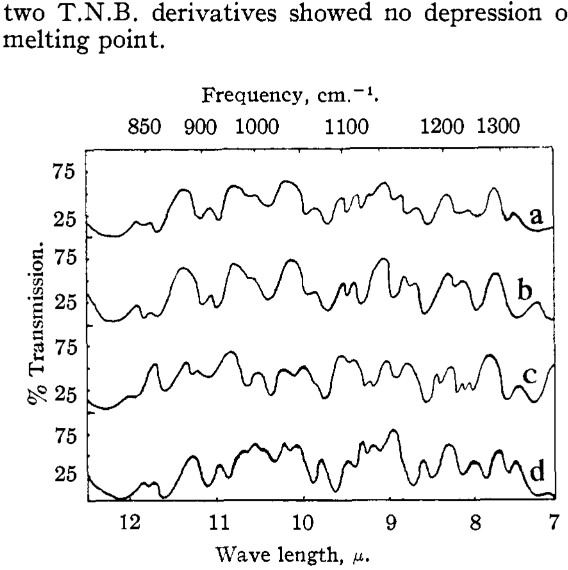

Fig. 1.—Infrared transmission spectrograms (0.178-mm. cell thickness) of the hydrogenation product from IX (a): 1-methylperinaphthane (b); 7-methylperinaphthane (c); and 3-methylperinaphthane (d).

In order to establish that rearrangement had not occurred in the hydrogenolysis experiment, the other two possible methylperinaphthanes were prepared by hydrogenolysis of III and VI. The 3-methylperinaphthane and 7-methylperinaphthane, thus produced, proved to be new and different hydrocarbons. This was established by their infrared absorption curves (see Fig. 1) and by the formation of their T.N.B. derivatives. It is therefore clear that the dihydro compound must be 1-methylperinaphthane and consequently the product of dehydration is 1-(or 6-)-methylperinaphthene (IX) with the position of the peri double bond being uncertain.

It would be of interest to know the position of the double bond in the peri ring, but attempts in this direction have been unsuccessful. The perinaphthenes, as has previously been noted,[6,8,9,10] are somewhat unstable compounds and no useful products have been obtained by oxidative procedures, although ozonolysis, treatment with per-acids, and various oxidizing agents have been employed.

The reason for the formation of IX in preference to the other possible isomers is not clear. Although it would be expected that hyperconjugation would favor a form having the methyl group attached directly to a fully aromatic ring, the isomeric 3-methylperinaphthene should be similarly stabilized. Since the dehydration step to form IX is acid catalyzed, it might be thought that the isomerization to IX is also promoted by

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[7] Buu-Hoï and Cagniant, *Rev. sci.*, **80**, 271 (1943).

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

[9] Lock and Gergely, *Ber.*, **77**, 461 (1944); also see ref. 2.

[10] Buu-Hoï and Cagniant, *Compt. rend.*, **216**, 346 (1943).

acid.[11] The isomerization of perinaphthenes by means of strong base, as originally planned, might therefore convert IX to a different isomer or mixture of isomers. However, when IX was converted to its anion with phenyllithium and the resulting solution was hydrolyzed with water, the original hydrocarbon was recovered in greater than 90% yield.

Two other experiments were carried out which also demonstrate the singular ease with which IX is formed in preference to the other possible isomers. Alkylation of perinaphthene (VIII) with phenyllithium and methyl iodide gave IX in 83% yield.[12] Since the initial product of this reaction must be 9-methylperinaphthene, isomerization occurred even though no acid was present and no temperature higher than that of boiling ether was attained. Finally, the reaction of methylmagnesium iodide with perinaphthenone (VII), which Craig, Jacobs and Lavin have reported as yielding a methylperinaphthene,[8] was repeated and found to give IX. This peculiar reaction appears to parallel the reaction of lithium aluminum hydride with perinaphthenone, for in addition to IX the other products of the reaction are methane and a compound having the correct composition for a methylperinaphthenone.

Since all syntheses designed to put a methyl group at the 1-, 3-, 6-, 7- and 9- positions of the perinaphthene ring invariably gave IX, it was of interest to see if a similar behavior would be found in the corresponding series of methylperinaphthenes where the positions possible for the methyl group are 2-, 5- and 8-. For this study 8-methylperinaphthanone-7 was prepared as previously described[13] and was reduced with lithium aluminum hydride to the corresponding carbinol, X. Dehydration of X gave 8-methylperinaphthene (XI), as was shown by the fact that XI gave 8-methylperinaphthane on catalytic reduction. The infrared absorption curve of the 8-methylperinaphthane thus produced was identical within experimental error with that of the product of hydrogenolysis of 8-methylperinaphthanol-7 (see Fig. 2). In addition the T.N.B. derivatives and the ultraviolet absorption curves of the two samples were the same.[14]

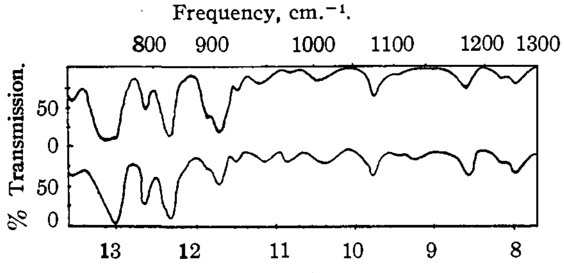
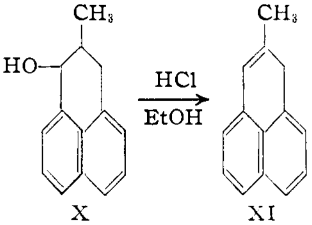


Fig. 2.—Infrared transmission spectrograms (0.025-mm. cell thickness) of the hydrogenation product from XI (a) and of 8-methylperinaphthane (b).



X XI

The fact that the dehydration of X gave 8-methylperinaphthene instead of 2- or 5-methyl-

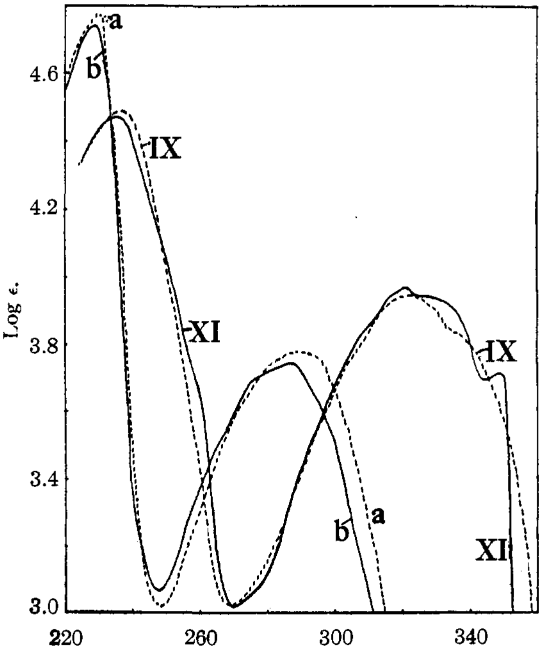


Fig. 3.—Ultraviolet absorption spectra of IX, XI, 1-methylperinaphthane (a), and 8-methylperinaphthane (b) in ethanol. Maxima and log ε values are: IX, 325 mμ (4.0) and 235 mμ (4.5); X, 348 mμ (3.7), 320 mμ (4.0) and 235 mμ (4.5); (a), 289 mμ (3.8) and 230 mμ (4.7); and (b), 287 mμ (3.8) and 229 mμ (4.8).

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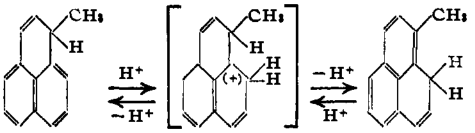
[11] A plausible mechanism for an acid-catalyzed isomerization can be written as is shown below:



[12] For a description of this experiment, see ref. 2.

[13] Fieser and Novello, THIS JOURNAL, 62, 1855 (1940).

[14] The preparation of 8-methylperinaphthane by the Clemmensen procedure has been reported by Fieser and Novello (ref. 13) who state that the T.N.B. derivative is reddish-brown and melts at 149–150°, dec. Our preparations of 8-methylperinaphthane gave a yellow T.N.B. derivative that melted at 138–140° without decomposition. It is possible that the T.N.B. derivative reported by Fieser and Novello is derived from 8-methylperinaphthene. In our experience all of the T.N.B. derivatives of the saturated perinaphthanes have been yellow and have melted without decomposition. It would seem that the formation of mixtures in the Clemmensen reduction is general for the perinaphthane series.

perinaphthene was somewhat surprising in view of the previous results. An attempt was therefore made to effect basic isomerization of XI. However, on treatment with phenyllithium followed by hydrolysis, XI was recovered practically quantitatively. It would appear that in this series 8-methylperinaphthene is the most stable member.

A comparison of the ultraviolet absorption spectra of IX, XI, 1-methylperinaphthane and 8-methylperinaphthane is given in Fig. 3. It is interesting that IX and XI have very similar curves, indicating that whether the methyl group is at the 8-position or at the 1-(or 6)- position has little effect on the absorption. All of the preparations of IX gave the same ultraviolet absorption curve and our curve agrees closely with that reported by Craig, Jacobs and Lavin.[8]

Although no case of isomerization by base was established in this study, the possibility that the symmetry of the perinaphthenyl nucleus is an important factor in the stability of ions or radicals derived from it is not discredited. It would seem, rather, that in the methylperinaphthene series isomerization occurs so readily that under the usual conditions only the most stable isomer can be isolated. No good explanation can be offered as to why IX and XI should be the most stable isomers of their respective series. It is probable that with some substituent group other than methyl, more than one isomer of a series could be isolated.

Experimental[15]

7-Methylperinaphthanol-7 (III).—This was prepared as described by Fieser and Newton.[6]

1-Methylperinaphthanol-7 (IV).—The preparation of 1-methylperinaphthanol-7 was accomplished in the following way. Chloromethylation of β-methylnaphthalene, according to the general procedure of Coles and Dodds,[16] gave a 68% yield of 1-chloromethyl-2-methylnaphthalene, b. p. 118–122° at 0.5 mm.[17] The conversion of the chloromethyl derivative to β-(1-(2-methyl)-naphthyl)-propionic acid was done as described by Klyne and Robinson.[3] The acid was then cyclized in 98% yield to 1-methylperinaphthanone-7 by the usual procedure with hydrogen fluoride.[4] The reduction of 1-methylperinaphthanone-7 to 1-methylperinaphthanol-7 occurred in 97% yield using lithium aluminum hydride as described previously for the reduction of perinaphthanone-7.[2] The over-all yield on the six-step synthesis was 43%.

3-Methylperinaphthanol-7 (VI).—The preparation of 3-methylperinaphthanol-7 was carried through a similar series of steps as described for IV. Chloromethylation of α-methylnaphthalene by the procedure of Coles and Dodds[16] gave 1-chloromethyl-4-methylnaphthalene in 76% yield.[17] The chloromethyl derivative was converted to β-(1-(4-methyl)-naphthyl)-propionic acid in 42% yield in essentially the same manner as described by Buu-Hoï and Cagniant.[18] Cyclization of the propionic acid with hydrogen fluoride by the usual procedure[4] gave 3-methylperinaphthanone-7 in 82% yield as a yellow solid, m. p. 68–69°.[18]

The reduction of 3-methylperinaphthanone-7 was accomplished using lithium aluminum hydride as previously described[2] and gave 3-methylperinaphthanol-7 in 94% yield. This was obtained after crystallization from a benzene–hexane mixture as white needles, m. p. 107–108°. The over-all yield in the six-step synthesis was 25%.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.84; H, 7.07. Found: C, 85.16; H, 7.29.

Preparation of 9-Methylperinaphthanol-7 (V). (a) Ethyl β-(1-Naphthyl)-crotonate.—This was prepared by the Reformatsky reaction with α-acetylnaphthalene.[19] A solution of 20 g. of α-acetylnaphthalene, 25 g. of ethyl bromoacetate and 75 ml. of absolute benzene was added slowly to 8.0 g. of zinc foil. After a small amount of solution had been added, a crystal of iodine was added to start the reaction and then the rest of the solution was added dropwise at a sufficient rate to maintain gentle boiling. When all of the solution had been added (two hours), an additional 2 g. of zinc and 5 g. of ethyl bromoacetate was added. The reaction mixture was boiled under reflux for another hour and a half, then cooled, and hydrolyzed with dilute hydrochloric acid. The benzene layer was separated, washed with water, and the benzene was removed. The residual oil was heated on a steam-bath and subjected to a stream of dry hydrogen chloride for two hours. The oil was then taken up in ether, washed with water, dried, and the ether was removed. Distillation of the residue gave an initial fraction of 7.7 g. of α-acetylnaphthalene and a second fraction of 9.8 g. (35%) of a colorless oil, b. p. 128–138° at 0.5 mm.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.99; H, 6.71. Found: C, 80.40; H, 6.51.

(b) **β-(1-Naphthyl)-butyric Acid.**—A mixture of 9.6 g. of ethyl β-(1-naphthyl)-crotonate, 50 ml. of alcohol and 50 ml. of a 10% aqueous sodium hydroxide was boiled under reflux overnight. The solution was cooled and extracted with ether to remove any unchanged ester. Raney nickel catalyst (4 g.) was added and the solution was shaken at room temperature under hydrogen pressure of three atm. until one mole of hydrogen had been absorbed. After removal of the catalyst and acidification, 8.0 g. (95%) of β-(1-naphthyl)-butyric acid, m. p. 109–110°,[20] was obtained.

(c) **9-Methylperinaphthanone-7.**—A solution of β-(1-naphthyl)-butyric acid in 80 ml. of hydrogen fluoride was allowed to stand for three hours, after which all of the hydrogen fluoride had evaporated. The residual oil was taken up in ether, washed successively with water, aqueous sodium hydroxide, and water, and then the ether was removed. Addition of pentane caused crystallization of the residue and 6.0 g. (87%) of a light yellow solid was collected. After crystallization from a mixture of benzene and hexane, the product was obtained as white prisms, m. p. 62–64°.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.72; H, 6.17. Found: C, 85.84; H, 5.91.

(d) **9-Methylperinaphthanol-7.**—Reduction of 9-methylperinaphthanone-7 to give 9-methylperinaphthanol-7 was carried out as previously described for the reduction of perinaphthanone-7 and proceeded in 88% yield. After crystallization from aqueous alcohol, the product was obtained as fine white needles, m. p. 150–151°. The over-all yield in the six-step synthesis from α-acetylnaphthalene was 25%.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.84; H, 7.07. Found: C, 84.45; H, 6.90.

Dehydration of Alcohols III, IV, V and VI to Yield 1-(or 6)-Methylperinaphthene, IX.—The various alcohols shown by formulas III, IV, V and VI were dehydrated by the procedure described by Fieser and Newton.[6] The yields of IX varied from 44% for the dehydration of 3-methylperinaphthanol-7 (VI) to 80% for the dehydration of 7-methylperinaphthanol-7 (III). A typical dehydration reaction is described.

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

[16] Coles and Dodds, THIS JOURNAL, **60**, 853 (1938).

[17] Darzens and Levy, *Compt. rend.*, **202**, 73 (1936).

[18] Buu-Hoï and Cagniant, *Rev. sci.*, **79**, 644 (1941).

[19] St. Pfau and Ofner, *Helv. Chim. Acta*, **9**, 669 (1926).

[20] Cauquil and Barrera (*Compt. rend.*, **226**, 1282 (1948)) give 108°.

To a solution of 2.00 g. of 1-methylperinaphthanol-7 (IV) in 10 ml. of absolute alcohol there was added 10 ml. of a saturated solution of dry hydrogen chloride in ethanol. The mixture was boiled under reflux for fifteen minutes and was then poured into 50 ml. of water. The organic material was extracted with ether, dried and the ether was removed. The residual oil was taken up in pentane and chromatographed using alumina. From the colorless pentane eluate there was obtained 1.00 g. (55%) of hydrocarbon as white plates, m. p. 62.5–63.5°.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 92.99; H, 6.80.

The trinitrobenzene derivative of IX formed readily in alcohol and was obtained after crystallization from alcohol as fine orange needles, m. p. 135–136° dec.

Anal. Calcd. for $C_{20}H_{15}N_3O_6$: C, 61.09; H, 3.85. Found: C, 61.03; H, 3.73.

In each case the crude oil before chromatography also gave the same T.N.B. derivative as did the purified material, indicating that isomerization had not occurred during passage over the alumina.

The picrate of IX was obtained as brick red needles, m. p. *ca.* 170° dec.

It was also found that dehydration of 7-methylperinaphthanol-7 (III) occurred thermally. Attempted vacuum distillation of III gave IX in poor yield.

Formation of 1-(or 6)-Methylperinaphthene by the Reaction of Perinaphthenone with Methylmagnesium Iodide.—This was repeated essentially as described by Craig, Jacobs and Lavin[8] except that a gas collecting apparatus was attached to the reaction flask. From 2.0 g. of perinaphthenone there was obtained, after purification by chromatography over alumina, 200 mg. (10%) of white plates, m. p. 63–64°. Preparation of the T.N.B. derivative and also a comparison of this with the previous samples showed it to be IX.

Evolution of gas during the reaction was vigorous and amounted to somewhat more than one-half of a molar equivalent. Its behavior on combustion indicated it to be methane. In addition to IX another product was obtained from the column which, although not identified, appeared to be that described by Craig, *et al.*,[8] as melting at 87–88° and having the composition $C_{14}H_{20}O$.

1-Methylperinaphthane. (a) **By Hydrogenation of IX.**—A solution of 1.05 g. of IX in 60 ml. of methanol was treated with 100 mg. of platinum oxide catalyst and was shaken at room temperature under 3 atm. pressure of hydrogen. When hydrogenation was complete, the catalyst and solvent were removed and the residual oil was taken up in pentane. The pentane solution was purified by chromatography and from the colorless eluate there was obtained 1.0 g. (94%) of a colorless oil.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.27; H, 7.74. Found: C, 92.65; H, 7.64.

The trinitrobenzene derivative of 1-methylperinaphthane was obtained from alcohol as fine yellow needles, m. p. 147–149°.

Anal. Calcd. for $C_{20}H_{17}N_3O_6$: C, 60.75; H, 4.34. Found: C, 60.92; H, 4.43.

The dehydration products from III, IV and VI were shown in each case to behave as given above. The formation of the T.N.B. derivative, m. p. 147–149°, occurred in high yield and no other product could be isolated from the mother liquor.

(b) **Hydrogenolysis of 1-Methylperinaphthanol-7.**—A solution of 3.0 g. of 1-methylperinaphthanol-7 (IV) in 10 ml. of alcohol was shaken at 220–230° in the presence of copper chromite catalyst under an initial hydrogen pressure of 1500 lb. The product was isolated as described in (a) and there was obtained 1.78 g. (64%) of 1-methylperinaphthane as a colorless oil.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.27; H, 7.73. Found: C, 92.61; H, 7.66.

The T.N.B. derivative of this product melted at 146–148°, and a mixture of the T.N.B. derivatives from (a) and (b) showed no depression of melting point. The infrared and ultraviolet absorption curves of 1-methylperinaphthane from (a) and (b) are shown in Figs. 1 and 3.

(c) **Wolff-Kishner Reduction of 1-Methylperinaphthanone-7.**—The reduction of 1-methylperinaphthanone-7 was carried out according to the general procedure described by Huang-Minlon.[21] From 1.52 g. of ketone only a small amount of colorless oil was obtained, but this product gave a yellow trinitrobenzene derivative, m. p. 147–149°. A mixed melting point determination showed the T.N.B. derivative to be the same as that obtained from (a) and (b).

3-Methylperinaphthane.—High pressure hydrogenolysis of 3-methylperinaphthanol-7 was carried out as described under (b) above. From 4.0 g. of 3-methylperinaphthanol-7 there was obtained 3.08 g. (80%) of a colorless oil. The infrared absorption spectra of 3-methylperinaphthane is shown in Fig. 1.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.27; H, 7.73. Found: C, 92.29; H, 7.77.

The trinitrobenzene derivative of 3-methylperinaphthane was obtained from alcohol as fine yellow needles, m. p. 128–129°.[22]

Anal. Calcd. for $C_{20}H_{17}N_3O_6$: C, 60.75; H, 4.34. Found: C, 60.80; H, 4.00.

7-Methylperinaphthane.—High pressure hydrogenolysis of 7-methylperinaphthanol-7 was also carried out as described under (b) above. From 3.00 g. of 7-methylperinaphthanol-7 there was obtained 2.16 g. (78%) of 7-methylperinaphthane as a colorless oil. The infrared absorption specta of 7-methylperinaphthane is given in Fig. 1.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.27; H, 7.73. Found: C, 92.60; H, 7.50.

The trinitrobenzene derivative of 7-methylperinaphthane was obtained from alcohol as fine yellow needles, m. p. 125–126°.

Anal. Calcd. for $C_{20}H_{17}N_3O_6$: C, 60.75; H, 4.34. Found: C, 60.47; H, 4.24.

A mixture of the T.N.B. derivatives of 3-methylperinaphthane and 7-methylperinaphthane showed a definite depression of melting point.

Attempted Clemmensen Reduction of 9-Methylperinaphthanone-7.—A mixture of 2.0 g. of 9-methylperinaphthanone-7, 8 g. of amalgamated zinc, 21 ml. of methanol, 21 ml. of benzene and 5 ml. of concentrated hydrochloric acid was boiled under reflux for eight hours. During this time an additional 4 ml. of hydrochloric acid was added to the mixture. After the solution was decanted from the zinc, it was extracted with ether. The ethereal solution was washed with water, dried, and the ether was removed. The residual oil was taken up in pentane and purified by chromatography over alumina. The colorless oil, thus obtained, gave a trinitrobenzene derivative, which formed as orange needles, m. p. 134–135° dec., and appeared to be the same as the T.N.B. from IX. However, the oil was probably a mixture since, in another run, a fraction of the eluate from the column gave a T.N.B. derivative which formed as yellow needles, m. p. 122–124, and was presumably the T.N.B. derivative of 7-methylperinaphthane.

Attempted Oxidations of 1-(or 6)-Methylperinaphthene.—Ozonolysis of 1-(or 6)-methylperinaphthene (IX) using carbon tetrachloride as solvent gave some acidic material, which was water soluble, but no useful product.

Treatment of IX with perbenzoic acid in chloroform proceeded quantitatively as indicated by titration, but attempts to isolate the epoxide were unsuccessful. Also attempts to utilize the epoxide without isolation in a Grignard reaction or a reaction with lithium aluminum hydride gave no useful product.

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[21] Huang-Minlon, This Journal, **68**, 248 (1946).

[22] Buu-Hoï and Cagniant (*Rev. sci.*, **80**, 130 (1942)) reported the preparation of 3-methylperinaphthane by the Clemmensen reduction and gave the T.N.B. derivative as decomposing above 120°.

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.

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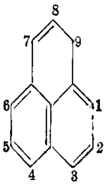
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

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-



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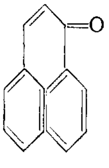

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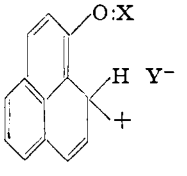
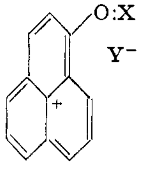


III



IV

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[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).