[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

# Dicyclic Hydrocarbons. VIII. 1-Alkylnaphthalenes and Some of their Tetrahydro Derivatives[1]

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Physical properties (boiling points, refractive indices, densities, heats of combustion and kinematic viscosities at four different temperatures) are presented for seven 1-alkylnaphthalenes and eight of their tetrahydro derivatives. Melting points and estimated purities are also given for the compounds that crystallize. The hydrocarbons were synthesized by well-known methods and were purified by precision fractional distillations to a purity in the order of 99 mole per cent. Three of the compounds, 5-butyltetralin, 1-isobutyltetralin and 5-isobutyltetralin, are described for the first time.

As part of an investigation of hydrocarbons for possible components of aviation fuels, a series of alkylnaphthalenes and their hydrogenated derivatives has been prepared. Several 1-alkyl-1,2,3,4-tetrahydronaphthalenes are described in a recent publication from this Laboratory.[2] Some excellent work has been published[3,4] on the preparation and properties of the *n*-alkylnaphthalenes reported herein. The best work of the 5-alkyl-1,2,3,4-tetrahydronaphthalenes is the separation of 5-methyltetralin from petroleum by Mair and Streiff.[5]

In the present investigation, the 1-alkylnaphthalenes were prepared by the condensation of appropriate reagents with 1-naphthylmagnesium bromide to yield the desired hydrocarbons or an intermediate which could easily be converted to the hydrocarbon.

The tetrahydro derivatives of 1-methyl-, 1-ethyl-, 1-butyl- and 1-isobutylnaphthalene were prepared by hydrogenation of purified 1-alkylnaphthalenes over copper chromite catalyst, and separation of the two resulting isomers by fractional distillation. The isomers were identified by a comparison of their physical properties with those already reported in the literature.[2,5,6] The three hydrocarbons not previously reported were identified by analogy; *i.e.*, the 1-alkyl-1,2,3,4-tetrahydronaphthalene is the lower-boiling isomer.

The syntheses were planned on a scale that was expected to yield a 500-ml. quantity of each hydrocarbon of a purity of at least 99 mole per cent. The final purification of the compounds consisted of fractional distillations in 6-ft. Podbielniak columns *in vacuo*. The individual fractions were passed through columns of silica gel or were freshly distilled prior to the determination of physical constants. Fractions were combined on the basis of constant melting-point values except with those compounds that did not crystallize. In those cases, constant refractive index and density were used as a basis for combining fractions.

TABLE I

PHYSICAL PROPERTIES, YIELDS AND ANALYSES OF 1-ALKYLNAPHTHALENES AND 1- AND 5-ALKYLTETRALINS

| | M.p., °C. | B.p., °C. at 760 mm. | $n^{20}\mathrm{D}$ | $D^{20}$, g./ml. | $\Delta H_f$, kcal./mole | Est. purity, mole % | Heat of comb., kcal./mole | Analyses, % Carbon | | Analyses, % Hydrogen | | Kinematic viscosity, centistokes | | | | Yield of const., $n^{20}\mathrm{D}$ material, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Calcd. | Found | Calcd. | Found | 210° F. | 140° F. | 100° F. | 32° F. | |
| Naphthalenes | | | | | | | | | | | | | | | | |
| 1-Methyl- | −30.50 | 244.42 | 1.6174 | 1.02015 | 2.3 | 99.9 | 1345 | 92.91 | 92.92 | 7.09 | 7.13 | 0.92 | 1.51 | 2.21 | 5.99 | .. |
| 1-Ethyl- | −13.88 | 258.67 | 1.6062 | 1.00816 | 3.9 | 99.8 | 1475 | 92.26 | 92.20 | 7.74 | 7.80 | 0.99 | 1.68 | 2.57 | 7.83 | .. |
| 1-Propyl- | − 8.60 | 272.78 | 1.5923 | 0.98970 | 4.2 | 99.6 | 1630 | 91.71 | 91.66 | 8.29 | 8.30 | 1.11 | 2.00 | 3.20 | 11.48 | .. |
| 1-Isopropyl- | −15.66 | 267.79 | 1.5952 | .99565 | 3.4 | 99.7 | 1630 | 91.71 | 91.65 | 8.29 | 8.27 | 1.11 | 2.00 | 3.20 | 11.88 | .. |
| 1-Butyl- | −19.76 | 289.34 | 1.5819 | .97673 | 6.0 | 99.8 | 1775 | 91.25 | 91.29 | 8.75 | 8.75 | 1.28 | 2.37 | 3.95 | 15.86 | .. |
| 1-Isobutyl- | − 9.37[a] | 279.54 | 1.5794 | .97144 | 5.4 | 99.8 | 1770 | 91.25 | 91.28 | 8.75 | 8.80 | 1.32 | 2.55 | 4.42 | 23.53 | .. |
| 1-Pentyl- | −24.54 | 305.15 | 1.5726 | .96609 | 5.6 | 99.2 | 1920 | 90.85 | 90.79 | 9.15 | 9.19 | 1.48 | 2.86 | 4.96 | 22.74 | .. |
| Tetralins | | | | | | | | | | | | | | | | |
| 1-Methyl- | Glass | 220.46 | 1.5354 | 0.95850 | ... | .. | .. | ... | ... | ... | ... | .. | .. | .. | ... | 21 |
| 5-Methyl- | −23.05 | 234.20 | 1.5440 | .97106 | 3.4 | 99.8 | 1425 | 90.35 | 90.38 | 9.65 | 9.68 | 0.93 | 1.52 | 2.22 | 5.81 | 64 |
| 1-Ethyl- | Glass | 239.40 | 1.5316 | .95290 | ... | .. | .. | ... | ... | ... | ... | .. | .. | .. | ... | 23 |
| 5-Ethyl- | −44.55 | 248.02 | 1.5398 | .96286 | 4.1 | 99.9 | 1570 | 89.93 | 89.85 | 10.07 | 10.11 | .99 | 1.62 | 2.40 | 6.37 | [b] |
| 1-Butyl- | Glass | 273.06 | 1.5220 | .93501 | ... | .. | .. | ... | ... | ... | ... | .. | .. | .. | ... | 10 |
| 5-Butyl- | −49[c] | 279.91 | 1.5280 | .94093 | ... | .. | 1860 | 89.29 | 89.22 | 10.71 | 10.72 | 1.31 | 2.40 | 3.93 | 14.95 | 56 |
| 1-Isobutyl- | Glass | 266.31 | 1.5198 | .93080 | ... | .. | 1850 | 89.29 | 89.41 | 10.71 | 10.72 | 1.14 | 2.01 | 3.18 | 11.37 | 15 |
| 5-Isobutyl- | −14.75 | 270.41 | 1.5269 | .93776 | 4.4 | 99.8 | 1860 | 89.29 | 89.29 | 10.71 | 10.69 | 1.34 | 2.57 | 4.43 | 21.80 | 62 |

[a] A second unstable crystalline modification melts at −22.14°. [b] Undetermined amount was lost when distillation column flooded. [c] Melting curve was too short to allow greater accuracy.

The physical properties of the hydrocarbons are listed in Table I. The melting points, boiling points, refractive indices, densities, net heats of combustion, heats of fusion and kinematic viscosi-

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(1) Presented in part before the Organic Division of the American Chemical Society in Cleveland, Ohio, April, 1951.

(2) W. Karo, R. L. McLaughlin and H. F. Hipsher, THIS JOURNAL, **75**, 3233 (1953).

(3) (a) S. H. Morrell, G. B. Pickering and J. C Smith, *J. Inst. Petr.*, **34**, 677 (1948); (b) A. S. Bailey, G. B. Pickering and J. C. Smith, *ibid.*, **35**, 103 (1949).

(4) H. Luther and G. Wachter, *Chem. Ber.*, **82**, 161 (1949).

(5) B. J. Mair and A. J. Streiff, *J. Research Natl. Bur. Standards*, **27**, 343 (1941).

(6) W. M. Kutz, J. E. Nickels, J. J. McGovern and B. B. Corson, THIS JOURNAL, **70**, 4026 (1948).

ties at four selected temperatures were determined by procedures previously referenced.[7] The values of the purity were determined by the method of Glasgow, *et al.*[8]

## Experimental

**Naphthalenes.**—The 1-alkylnaphthalenes were prepared by the condensation of appropriate reagents with 1-naphthylmagnesium bromide to yield the desired hydrocarbon or an intermediate which could easily be converted to the hydrocarbon. Dimethyl and diethyl sulfate were employed for the synthesis of 1-methyl- and 1-ethylnaphthalene as reported in reference 9. 1-Isopropylnaphthalene was synthesized by using acetone as the condensing agent, dehydration of the intermediate carbinol, and catalytic hydrogenation of the resulting olefin. 1-Isobutylnaphthalene was prepared by the hydrogenation of the olefin resulting from the condensation of methallyl chloride with the Grignard reagent. Several methods were used for the synthesis of 1-propyl-, 1-butyl- and 1-pentylnaphthalene; the most successful was the use of the appropriate nitrile for the condensing agent, hydrolysis to the ketone, and an atmospheric pressure Wolff–Kishner reduction[10] of the ketone to the hydrocarbon.

Each of the alkylnaphthalenes was found to be contaminated with a hydrocarbon impurity presumed to be the 2-isomer. The impurity, in the case of 1-ethylnaphthalene, was identified as the 2-isomer by infrared analysis.[6] It was found that the desired 1-isomer could be purified by fractional distillation in all cases, but purification was extremely difficult with the propyl compounds. The 2-isomers of methyl- and ethylnaphthalene have lower boiling points than the corresponding 1-isomers[8] and are removed in the forerun of the distillation. However, the 2-isomers of the propyl- and butylnaphthalenes have boiling points higher than those of the corresponding 1-isomers,[8] and are therefore concentrated in the undistilled portion of the charge. Thus, the mole fraction of the impurity is constantly increasing in both the liquid and vapor phases, making the purification increasing difficult as the distillation progresses. Several fractional distillations of 1-propylnaphthalene and 1-isopropylnaphthalene were required before the desired purity was attained.

**Tetralins.**—The 1- and 5-alkyltetralins were prepared by catalytic hydrogenation of purified 1-alkylnaphthalenes. The quantity of each hydrocarbon hydrogenated varied according to the amount available for such use. The hydrogenations were carried out in a 4.5-liter rocking autoclave at 1500–2000 p.s.i. and 195–225° in the presence of approximately 10% by weight of a barium-promoted copper chromite catalyst. Essentially quantitative yields of product were obtained after de-adsorption of the catalyst with boiling ethanol.

The isomers were separated by fractional distillation in 6-ft. Podbielniak columns at 100 mm. for the methyl and ethyl compounds and at 20 mm. for the butyl compounds. The ratio of the amounts of 1-isomer and 5-isomer formed in the hydrogenation was 1.3 in every instance except for the ethyl derivative. After 1-ethyl-1,2,3,4-tetrahydronaphthalene had been distilled from the mixture, the distillation column flooded over, and an undetermined amount of the 5-isomer was lost. The ratio of 1.3 was calculated on the basis of the amounts of constant $n^{20}\mathrm{D}$ material obtained plus an estimation of the amounts of each isomer in the intermediate fractions of the distillation based on the assumption that refractive indices are volume additive. The percentage yield of constant $n^{20}\mathrm{D}$ material of each compound is given in the table.

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

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

(9) H. Gilman and R. E. Hoyle, THIS JOURNAL, **44**, 2621 (1922).

(10) (a) M. D. Soffer, M. B. Soffer and K. W. Sherk, *ibid.*, **67**, 1435 (1945); (b) C. H. Herr, F. C. Whitmore and R. W. Schiessler, *ibid.*, **67**, 2061 (1945).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

# Reactions of Hindered α-Substituted Succinic Acids. II. Structure of the Rearranged Acids[1]

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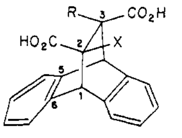
Evidence for the structures and configurations of the products of the acid-induced rearrangement of 2-hydroxy-3-methyldibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid (I) and the alkali-induced rearrangement of 2-bromodibenzo[2,2,2]-bicycloöctadiene-*trans*-2,3-dicarboxylic acid (II) is presented. It is also shown that silver nitrate can effect an analogous rearrangement of II with the production of a lactone acid similar to that produced from I. The elimination of bromide with the β-carboxyl accompanies the silver nitrate induced rearrangement, though to a lesser extent than observed in the alkali-induced rearrangement.

In a previous paper[3] there was reported the anomalous behavior of 2-hydroxy-3-methyldibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid (I) with hot 48% hydrobromic acid and of 2-bromodibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid (II) with alkali. Evidence was presented to support the hypothesis that any external nucleophilic attack upon carbon 2 was highly improbable, if not actually impossible, owing to steric factors. Thus any displacement of a group attached at this position must be a consequence of intramolecular nucleophilic attack. The formation of dibenzo[2,2,2]bicycloöctatriene-2-carboxylic acid from II by treatment with alkali was explained on this basis. However, speculation as to the nature of the hydroxy dibasic acid IV produced simultaneously and of the lactone acid III, which was the only product obtained upon reaction of I with 48% hydrobromic acid at 100°, was deferred until additional evidence was available. It was, however, remarked that anthraquinone was produced upon permanganate oxidation of IV while no anthraquinone was obtained from III under similar conditions. On the basis of these data it was suggested that Wagner–Meerwein rearrangements had occurred in both reactions, since both III and IV were oxidizable under relatively mild conditions whereas I and II were not; and it was further suggested on the



I, X = OH, R = $CH_3$
II, X = Br, R = H

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(1) Abstracted in part from a portion of the Ph.D. dissertation of Randel Q. Little, Jr., University of Michigan, 1953.

(2) American Brake Shoe Company Fellow, 1952–1953.

(3) W. R. Vaughan and K. M. Milton, THIS JOURNAL, **74**, 5623 (1952).