[Contribution from the School of Chemistry of the University of Minnesota]

STUDIES IN THE PERINAPHTHENE¹ SERIES. IV². SOME ATTEMPTS TO SYNTHESIZE 9-PHENYL-PERINAPHTHANONE-7

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Some time ago it was reported (1) that cyclization of β -phenyl- β -(2methoxynaphthyl)propionyl chloride with aluminum chloride led to 1-methoxy-9-phenylperinaphthanone (I). Although the analytical figures for the product and for its derivatives were in agreement with this formula, other considerations made it possible that the cyclization was accompanied by dehydrogenation and that the product might be a perinaphthenone derivative. The compound has now been found to yield a benzal derivative (II) when treated with benzaldehyde and alkali, and accordingly its structure is definitely that indicated by the analyses.



With the perinaphthanone structure (I) established, it was desirable to investigate the chemical behavior of the parent ketone III to discover if certain peculiarities of I were also found in the methoxyl-free substance. But none of the syntheses attempted for the preparation of III have yielded this compound. Some attempts which gave results of general interest are described in the present paper.

¹ The general title for the papers in this series and the naming and numbering of the compounds concerned have been changed in accordance with recent suggestions on nomenclature (9).

² Paper III, KOELSCH AND ROSENWALD, J. Org. Chem., 3, 462 (1938).

³ Abstracted from a thesis by J. A. Anthes presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the Ph.D. degree, January, 1939.



Treatment of cinnamoylnaphthalene (IV) with aluminum chloride has been reported (2) to yield III, but it is now shown that the substance obtained in this way is actually perinaphthenone-7 (V). The synthesis appears to hold some promise as a general method for preparing perinaphthanones, since 1-cinnamoyl-2-methoxynaphthalene (VI) can be converted through an intermediate (VIII) in satisfactory yield into 6-hydroxynaphthenone-7 (VII).

Considered in analogy with the results of Fuson (3) on the reversibility of the Friedel-Crafts reaction and with those of Koelsch and Richter (4) on aromatization through elimination of hydrocarbons from hydroaromatic rings, the elimination of benzene in the present instance is not surprising. However no reasonable hypothesis can be advanced to explain why benzene is not eliminated from I either when this substance is formed or when it is heated with an excess of aluminum chloride.

Another reaction which might have led to III is the one between phenylmagnesium bromide and perinaphthenone-7 (V).



The product here, however, is IX, since its dehydrogenation by distillation leads to a phenylperinaphthenone (X) which can be oxidized to the known (5) 2-phenylnaphthalic anhydride. The Grignard reaction thus, in spite of the absence of substituents in the 8 and 9 positions of V, involves the 6,6a rather than the 8,9 double bond of this ketone. It is of the same type as a number of previously studied (5) Grignard additions to perinaphthenones.

Finally it was hoped that III could be prepared by reduction of 9-phenylperinaphthenone (XI), a ketone which was obtained from 1-benzoylnaphthalene through β -(1-naphthyl)cinnamic acid. The reduction, however, does not involve the 8,9 double bond; it proceeds in two separate stages, in each of which one atom of hydrogen is taken up. The first product (XII), a crystalline red substance, shows a molecular weight in



melted camphor corresponding to a monomeric radical or semiquinone. But this low molecular weight is considered to be due to disproportionation into XI and XIII, for a solution made from XII in acetic acid has a color whose depth is inversely proportional to dilution. As pointed out by Michaelis (6), such colorimetric measurements can be used to distinguish between semiquinone and dimer formation, since in the former case $K = \frac{(S)^2}{(T)(R)}$ and in the latter $K = \frac{D}{(T)(R)}$ where T represents an oxidized form, R a reduced form, S a semiquinone, and D a dimer.

The second product (XIII) is a colorless solid. It reacts readily with oxygen to give XII and later XI, but this reconversion to XI is not quantitative; non-crystalline by-products are formed, and more oxygen is taken up than is necessary for oxidation to XI. 9-Phenylperinaphthenone-7 (XI) reacts with an equivalent amount of XIII in ligroin to give XII quantitatively.

At the dropping mercury electrode,⁴ XI is reduced, the two reduction potentials found corresponding to the two stages in the process. The curve obtained (Fig. 1) coincides with the one obtained similarly for peri-

⁴ We are indebted to Dr. James Lingane for assistance in experiments involving the dropping electrode.



Fig. 1. Reduction of 9-phenylperinaphthenone-7 in 0.1 N LiCl in 65% Ethanol, T = 25° , at the Dropping Mercury Electrode



Fig. 2. Reduction of Perinaphthenone in 0.1 N LiCl in 50% Ethanol, T = 26°, at the Dropping Mercury Electrode

naphthenone-7⁵ (V) (Fig. 2). This supports the structures already advanced for the reduction products, since if reductioninvolved the 8,9 double bond, the phenylated substances (XI and XII) would have reduc-(ion potentials different from those of the non-phenylated substances tV and its quinhydrone).

EXPERIMENTAL

8-Benzal-1-methoxy-9-phenylperinaphthanone-7 (II). To a solution of benzaldehyde (1 g.), 1-methoxy-9-phenylperinaphthanone-7 (1) (0.2 g.) and sodium hydroxide (5 drops of 40%) in alcohol (15 ml.) was added enough water to cause incipient precipitation. The whole was heated on a steam-bath for twelve hours and then cooled. Treatment of the precipitated oil with alcohol left a solid which was recrystallized from benzene. The product (0.05 g.) formed pale yellow crystals that melted at 168-170°; it gave a deep blue color with concentrated sulfuric acid.

Anal. Calc'd for C₂₇H₂₀O₂: C, 86.2; H, 5.4.

Found: C, 86.4; H, 5.4.

Perinaphthenone-7 (V). (a) From 1-cinnamoylnaphthalene. The Friedel-Crafts reaction between naphthalene (200 g.) and acetyl chloride (200 g.) in carbon disulfide gave a mixture of 1- and 2-acetylnaphthalene boiling at 154–156° (10 mm.), in a yield of 94%. This was separated by treatment with picric acid (7), a yield of 44% of pure 1-acetylnaphthalene being obtained.

A mixture of this ketone (88 g.) and benzaldehyde (64 g.) with a solution of sodium hydroxide (30 g.) in water (270 ml.) and alcohol (190 ml.) was stirred at $15-25^{\circ}$ for five hours and finally heated on a steam-bath for a few minutes. On standing, the mixture deposited 1-cinnamoylnaphthalene as a yellow oil which was not obtained crystalline (literature (8), m.p. 105°). A portion of this oil (50 g.) with aluminum chloride (100 g.) in carbon disulfide (200 ml.) was boiled for two hours. The mixture was hydrolyzed with iced hydrochloric acid, and the product was crystallized from benzene-ligroin and then from dilute alcohol. It formed brownish plates (9.4 g.) that melted at 152-154°. An additional crystallization from ligroin gave yellow plates that melted at 153.5-154° alone or mixed with an authentic sample (literature (9), corr. m.p. 156-156.5°).

(b) From cinnamic acid and naphthalene. A solution of cinnamic acid (40 g.) and naphthalene (40 g.) in benzene (500 ml.) was treated with phosphorus pentachloride (80 g.) and boiled for five minutes. Aluminum chloride (112 g.) was added in portions with cooling, and the whole was then boiled for twenty-five minutes. The aluminum complex was decomposed with iced hydrochloric acid, and the perinaphthenone was extracted from the tarry material in the benzene by washing twice with conc'd hydrochloric acid. It was precipitated by dilution with water and crystallized from benzene; yield, 6 g.

1-Cinnamoyl-2-methoxynaphthalene. A mixture of cinnamic acid (70 g.), 2-methoxynaphthalene (70 g.), phosphorus pentachloride (100 g.), and benzene (400 ml.) was boiled for five minutes, then cooled and treated with aluminum chloride (70 g.) added in small portions. The deep red solution was boiled for ten minutes and then

⁵ Reduction of perinaphthenone-7 with zinc and acetic acid was accompanied by color changes similar to those shown by 9-phenylperinaphthenone-7 [cf. Fieser and Hershberg, J. Am. Chem. Soc., **60**, 1660 (1938)] but the compounds involved could not be isolated in pure states.

decomposed with iced hydrochloric acid. The benzene was steam distilled and the residue was crystallized from a mixture of chloroform and alcohol. The product (92 g.) formed bright yellow needles that melted at $140-141^{\circ}$ (literature (10), $138-140^{\circ}$).

The ketone was also prepared from 1-acetyl-2-methoxynaphthalene and benzaldehyde, but this synthesis was more tedious than that described above.

5,6-Benzoflavanone (VIII). A mixture of 1-cinnamoyl-2-methoxynaphthalene (20 g.), carbon disulfide (150 ml.), and aluminum chloride (10 g.) was stirred at room temperature for four hours, allowed to stand overnight and then worked up in the usual way. The product was separated by crystallization from acetic acid into unchanged cinnamoylnaphthalene (4 g.) and 5,6-benzoflavanone [VIII, 2,3-dihydro-3-phenylnaphtho(2.1-b)pyrone-1, Ring Index No. 2004] (7 g.). The latter substance formed colorless plates that melted at 116-117°. It gave a red color with alcoholic alkali, a brownish-red with ferric chloride, but no test with Folin's reagent.

Anal. Calc'd for C₁₉H₁₄O₂: C, 83.1; H, 5.1.

Found: C, 83.0; H, 5.1.

With benzaldehyde and alcoholic alkali, 5,6-benzoffavanone gave a benzal derivative, pale yellow crystals that melted at 164-166°.

Anal. Calc'd for C₂₆H₁₈O₂: C, 86.2; H, 5.0.

Found: C, 86.0; H, 5.0.

6-Hydroxperinaphthenone-7 (VII). A mixture of 1-cinnamoyl-2-methoxynaphthalene (20 g.), benzene (300 ml.), and aluminum chloride (18 g.) was stirred and boiled for twenty-five minutes and then decomposed with iced hydrochloric acid. The benzene layer was separated, and hydrogen chloride was passed into it; the hydroxyperinaphthenone hydrochloride which precipitated was filtered and boiled with a mixture of alcohol and chloroform to set free the ketone. The product (8.2 g.) formed golden plates that melted at 200-201°. It formed a sodium salt difficultly soluble in water, and gave a fluorescent green solution in sulfuric acid.

Anal. Calc'd for C₁₃H₈O₂: C, 79.6; H, 4.1.

Found: C, 79.3; H, 3.9.

Unsuccessful attempts were made to methylate 6-hydroxyperinaphthenone-7 using the sodium salt and methyl sulfate, the silver salt and methyl iodide, and methanol and hydrogen chloride. Likewise all attempts to acetylate or to benzoylate the compound were unsuccessful.

With aqueous permanganate, first in alkaline then in acidic solution, 6-hydroxyperinaphthenone-7 (1.1 g.) gave the mono-potassium salt of hemimellitic acid (0.7 g.). The acid obtained from this salt melted at $191-192^{\circ}$ and with diazomethane gave a methyl ester which melted at $100-102^{\circ}$ alone or mixed with an authentic sample of trimethyl hemimellitate.

Addition of phenylmagnesium bromide to perinaphthenone. A solution of perinaphthenone-7⁶ (10 g.) in an excess of ethereal phenylmagnesium bromide was boiled for three hours and then decomposed with iced hydrochloric acid. The alkalisoluble oily product was dehydrogenated by distillation under reduced pressure and then crystallized from acetic acid. There was obtained 6.5 g. of 1-phenylperinaphthenone-7 (X) which melted at 145-147°, and on further crystallization at 150-

⁶ The ketone used in experiments summarized in this section was prepared both by the method previously described in this paper and by the method of Silberman and Barkov [J. Gen. Chem. U. S. S. R., 7, 1733 (1937)] using essentially the modifications described by Fieser and Hershberg (9).

152°. It formed orange-yellow crystals which were insoluble in alkali but which gave an orange-yellow solution with green fluorescence in sulfuric acid.

Anal. Calc'd for C₁₉H₁₂O: C, 89.0; H, 4.7.

Found: C, 89.1; H, 5.5.

Oxidized in acetone with potassium permanganate (2.5 g.), 1-phenylperinaphthenone-7 (1 g.) was partly recovered unchanged (0.6 g.) and partly converted into 2-phenylnaphthalic anhydride (0.13 g.) which melted at 237-239° alone or mixed with an authentic sample (5).

Synthesis of 9-phenylperinaphthenone-7. A mixture of 1-benzoylnaphthalene (220 g.), ethyl bromoace tate (160 g.), benzene (600 ml.), and granular zinc (60 g.) was warmed to start the reaction, and then boiled for six hours. Dilute hydrochloric acid was added, and the benzene layer was washed and evaporated. A portion of the residue was separated by crystallization from alcohol into 1-benzoylnaphthalene and ethyl β -hydroxy- β -(1-naphthyl)hydrocinnamate. The latter substance formed colorless cubes that melted at 116.5–118° and gave a bright green solution in sulfuric acid.

Anal. Calc'd for C₂₁H₂₀O₃: C, 78.8; H, 6.7.

Found: C, 78.5; H, 6.8.

A solution of ethyl β -hydroxy- β -(1-naphthyl)hydrocinnamate (1 g.) in concentrated sulfuric acid (10 ml.) was allowed to stand at room temperature for two hours and then poured into water. The solid was crystallized from ligroin, giving 9-phenylperinaphthenone-7 (0.3 g.) which melted at 142-143° (literature (11), 142-143°).

Anal. Calc'd for C₁₉H₁₂O: C, 89.0; H, 4.7.

Found: C, 88.8; H, 4.7.

The bulk of the product from the Reformatsky reaction was boiled with alcoholic potassium hydroxide to recover unchanged 1-benzoylnaphthalene (100 g.). Crude β -hydroxy- β -(1-naphthyl)hydrocinnamic acid was precipitated with hydrochloric acid and was cyclized without further purification. Twenty grams of the substance treated with 180 ml. of cold conc'd sulfuric acid gave 7 g. of 9-phenylperinaphthenone-7.

Reduction of 9-phenylperinaphthenone-7. To a solution of 9-phenylperinaphthenone-7 (2 g.) in acetic acid (25 ml.) and water (5 ml.) was added 0.7 g. of zinc dust. On shaking, the yellow mixture became red and then colorless. The zinc was filtered, and the mother liquor, which rapidly became red, was allowed to stand exposed to air for ten hours, when dark red crystals of 7,7'-bi-(4-phenyl-6-hydroxyperinaphthenyl) (XII) were deposited in good yield. From the mother liquor was recovered a small amount of 9-phenylperinaphthenone-7. Recrystallized from dilute alcohol, the red compound sintered at 124° and melted to a dark red liquid at 127-128°. A solution in melted camphor was orange.

Anal. Calc'd for C38H28O2: C, 88.7; H, 5.1; Mol. wt., 514.

Found: C, 88.3; H, 5.2; Mol. wt. (Rast), 257.

A colorless acetic acid solution obtained by reducing 0.4 g. of 9-phenylperinaphthenone-7 absorbed 15 ml. of oxygen in twenty-two hours and 30 ml. in one hundred hours (calc'd for 1 atom of oxygen per mole, 19.6 ml.). From the dark solution there was then isolated 0.31 g. of pure 9-phenylperinaphthenone-7 and some tarry material.

A column 1 cm. high of an acetic acid solution of XII, sufficiently concentrated that a definite red color was apparent, was placed in each of two colorimeter tubes. To one of these was added acetic acid to a height of 3 cm. The color in the more

dilute solution became orange; viewed through the whole length of the solution, the depth of color was approximately one-third that of the undiluted solution.

4-Phenyl-6-hydroxyperinaphthene (XIII) was obtained by carrying out the reduction of 9-phenylperinaphthenone-7 with zinc and acetic acid in an atmosphere of hydrogen. It was nearly colorless, melted at 136–138° and was soluble in aqueous sodium hydroxide. Since it rapidly became red in air, giving XII, it was not analyzed. Attempts to obtain derivatives by treating XIII with methyl sulfate and alkali, or with diazomethane, or by carrying out the reduction of XI in acetic anhydride-sulfuric acid gave negative results. A ligroin solution of XIII became red on mixing with one containing an equal weight of XI, and the quinhydrone XII was deposited in good yield.

SUMMARY

The structure of 1-methoxy-9-phenylperinaphthanone-7 has been substantiated by conversion of the substance into a benzal derivative, but attempts to synthesize the parent compound, 9-phenylperinaphthanone-7, have been unsuccessful. The attempts were (a) the cyclization of 1-cinnamoylnaphthalene, which gave perinaphthenone-7, (b) the treatment of perinaphthenone-7 with phenylmagnesium bromide, which gave 6-phenylperinaphthenone, and (c) the reduction of 9-phenylperinaphthenone, which gave 4-phenyl-6-hydroxyperinaphthene. The last named compound was of particular interest since it reacted with 9-phenylperinaphthenone-7 to form a quinhydrone.

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