carbonate removed 1.4 g. of 8-benzoylnaphthoic acid which, in agreement with the literature,[6] melted and decomposed at 110–115°. The ethyl ester of this acid, prepared with thionyl chloride, melted at 164–166° (literature[6] 166–167°).

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.95; H, 5.26. Found: C, 78.7; H, 5.03.

Oxidation of 7-phenylacenaphthenone also may be brought about by oxygen. A suspension of the ketone (1 g.) in 60 ml. of 10% alcoholic potassium hydroxide lost its color after standing exposed to air for twelve hours. The resulting solution, distilled to a small volume and acidified, yielded benzoylnaphthoic acid, identified by conversion into its ethyl ester.

Reaction with Phenylmagnesium Bromide.—A solution of 4 g. of phenylacenaphthenone in benzene (20 ml.) was added to a Grignard reagent prepared from 2.6 g. of bromobenzene. The yellow oil obtained on working up the reaction mixture could not be obtained crystalline, and accordingly was boiled for one hour with 100 ml. of 0.5% sulfuric acid in acetic acid. On cooling, this solution deposited diphenylacenaphthylene (2.7 g.) in the form of orange needles that melted at 164.5–166° (literature,[7] 159.5–161°).

Anal. Calcd. for $C_{24}H_{16}$: C, 94.7; H, 5.26. Found: C, 94.9; H, 5.44.

On treatment with chromic acid in acetic acid, this hydrocarbon gave 1,8-dibenzoylnaphthalene which melted at 186–188° (literature,[8] 189–190°).

Benzoylation.—The benzoate of 7-phenyl-8-hydroxyacenaphthylene was obtained in good yield by adding a slight excess of benzoyl chloride to a solution of phenylacenaphthenone in dry pyridine, adding enough chloroform to dissolve the precipitate formed, and warming the resulting solution to 60° for one hour. It separated from benzene–ligroin in rosets of orange needles that melted at 143–145°.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.2; H, 4.56. Found: C, 86.15; H, 4.6.

Attempted Methylation.—A boiling solution of the ketone (0.5 g.) in methanol (15 ml.) containing methyl sulfate (1 ml.) was treated dropwise with 5% alcoholic potassium hydroxide until the red color was permanent. More methyl sulfate was added, followed by alkali, but although this procedure was repeated several times a point was never reached where the addition of alkali failed to restore the red color. Only unchanged ketone could be isolated.

Summary

When treated with aluminum chloride, phenyl-α-naphthylacetyl chloride yields 7-phenylacenaphthenone, a substance which exists in its ketonic form.

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(6) Mason, *J. Chem. Soc.*, **125**, 2119 (1924).

(7) Wittig, Leo and Wiemer, *Ber.*, **64**, 2405 (1931).

(8) Veschke, *Ann.*, **369**, 201 (1909).

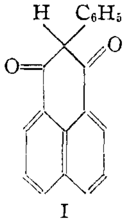
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies in the *peri*-Naphthindene Series. II. The Action of Phenyl-lithium on 8-Phenyl-*peri*-naphthindandione-7,9[1]

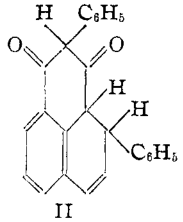
BY C. F. KOELSCH AND R. H. ROSENWALD

In continuing the program outlined in paper I of this series[2] it was planned to compare the reactions of 2,3-diphenylindone with those of the unknown 7,8-diphenyl-*peri*-naphthindone. It was hoped that the latter substance could be obtained from 8-phenyl-*peri*-naphthindandione-7,9 (I) and phenyl-lithium, through a reaction similar to that used for the preparation of a number of disubstituted indones[2] (p. 1328).

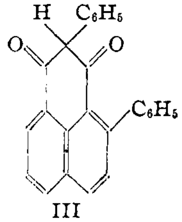
It was apparent, however, that the product which resulted from this reaction, although having the proper composition, was not the expected hydroxy ketone, since it was soluble in alkali and could not be dehydrated. A further study of the substance has led us to consider it as an enol of 1,8-diphenyl-1,9-α-dihydro-*peri*-naphthindandione-7,9 (II).



I



II



III

The formation of this compound undoubtedly involves the enol of I and in some respects is analogous to the previously observed 1,4-addition of Grignard reagents to benzanthrone. That the primary 1,4-addition product can be isolated in the present instance is of unusual interest, for in all similar reactions so far reported, the addition product has been isolated only after it has become aro-

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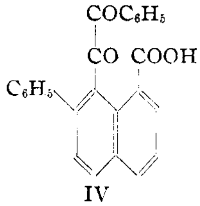
[1] Abstracted from the thesis of R. H. Rosenwald, submitted to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, December, 1936.

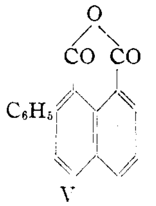
[2] Koelsch, THIS JOURNAL, **58**, 1326 (1936).

matic through rearrangement or the spontaneous loss of hydrogen.

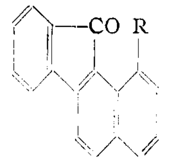
The formulation of II as a 1,4-addition product is based on the data obtained through oxidation. The first step in this oxidation, dehydrogenation to 1,8-diphenyl-*peri*-naphthindandione-7,9 (III) may be carried out in several ways, best by the use of benzoquinone. The product, III, treated with alkaline permanganate yields an acidic substance, IV, which, although it differs from most α-diketones in being colorless and in failing to form a quinoxaline, is nevertheless given this structure because it forms a yellow sodium salt and is cleaved by alkaline hydrogen peroxide. The position of the phenyl on carbon 7 of the naphthalene nucleus is only assumed, since it might equally well be on carbon 2, and all experiments designed to ascertain this part of the structure of IV have given inconclusive results. By the action of alkaline hydrogen peroxide or of chromic acid, IV is oxidized to benzoic acid and the anhydride of 2-phenylnaphthalene-1,8-dicarboxylic acid, V. Cyclization of the anhydride with aluminum chloride yields chrysoketone-10-carboxylic acid, VI, and decarboxylation of this gives the known 1,2-benzofluorenone, VII. The formation of this ketone can be accounted for only if the original addition product, II, contains a 1-phenyl group.



IV

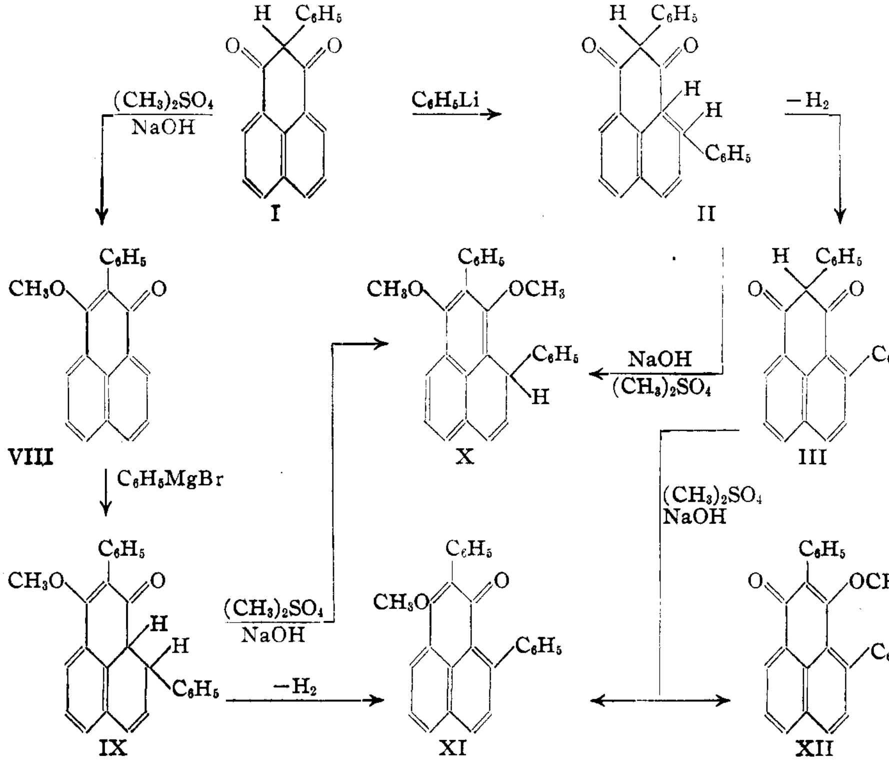


V



VI, R = COOM
VII, R = H

A study of the methyl derivatives of the diketones involved in this research has also given results in accord with the structures suggested. This study is summarized in the accompanying formulas.



Since I is symmetrical and can enolize only once, it gives only a single monomethyl ether (VIII) on treatment with methyl sulfate and alkali. This substance (VIII), still containing a carbonyl group, adds one equivalent of phenylmagnesium bromide. The reaction must be one of 1,4-addition, since the product (IX) can be converted into the dimethyl ether (X), and (X) may also be obtained by the methylation of II, known to be a 1,4-addition product of I.

Unlike I, the diketone III is unsymmetrical, and on this account it gives two isomeric monomethyl ethers. Both of these can be isolated. One (m. p. 251°), since it is identical with the dehydrogenation product of IX, must be the 7-methoxy-9-keto compound, XI, and this leaves formula XII for the other isomer (m. p. 141°).

Experimental

8-Phenyl-*peri*-naphthindandione-7,9, I.—A mixture of phenylacetic acid (105 g.), naphthalic anhydride (130 g.) and potassium[3] acetate (60 g.) is heated at 210–230° for four hours. Extraction of the melt with warm dilute sodium hydroxide gives a solution from which, by saturation with sodium chloride and then with carbon dioxide, the crude diketone is obtained. Purified by crystallization from acetic acid, the product weighed 135 g. and melted at 214–216°.[4] The behavior of the diketone toward mineral acids is like that of its phenyl derivative (see below).

1,8 - Diphenyl - 1,9a - dihydro - *peri* - naphthindandione-7,9, II.—The mixture obtained by adding 108 g. of 8-phenyl-*peri*-naphthindandione to an ethereal solution of 1.2 mols of phenyl-lithium is stirred for three hours and allowed to stand overnight. It is then decomposed by adding water and acetic acid, and the solvent and biphenyl are removed by steam distillation. From the red, solid residue, by crystallization from acetic acid (600 ml.) and then from toluene–petroleum ether, is obtained 52 g. of the addition product, II, which melts at 170–175°. The mother liquors contain an additional amount of the product which cannot be separated profitably from unchanged starting material. After further crystallization the product forms a yellow powder which melts to a red liquid at 178.5°; it gives a yellow solution in 10% aqueous sodium hydroxide.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.68; H, 5.18. Found: C, 85.81; H, 5.26.

The use of phenylmagnesium bromide in place of the lithium compound gives, at 35°, only unchanged starting material. At 100° (toluene added) there is obtained mainly tar, together with a small amount of a red, alkali soluble substance that melts at 200–210°. Oxidation of the tar with potassium permanganate after dehydrogenation with air yields the diketo acid IV in an amount indicating the presence of 3% of II.

1,8-Diphenyl-*peri*-naphthindandione-7,9, III. (a) **Dehydrogenation with Quinone.**—To a toluene solution of 1 g. of the dihydro compound II is added 0.7 g. of benzoquinone. The quinhydrone which separates is filtered off after thirty minutes, and the solution extracted with 10% aqueous sodium hydroxide. By acidifying the alkaline extract and crystallizing the precipitate from toluene–ligroin there is obtained 0.6 g. of product (melting point 146–147°).

(b) **Dehydrogenation with Oxygen.**—The yellow solution of the dihydro compound II in 1% aqueous sodium hydroxide becomes red when air is passed through it for several hours. Acidification then yields the dehydrogenated substance (mixed melting point 145–147°). This method of dehydrogenation is useful when oxidation with permanganate is the next reaction to be carried out.

(c) **Thermal Dehydrogenation.**—The crude red solid (38 g.) left when the ether and diphenyl are removed from the hydrolyzed reaction mixture of phenyl–lithium and I on distillation at 15 mm. gives 21 g. of a red glass. This, dissolved in ether and treated with ligroin, yields 6 to 12 g. of the dehydrogenated diketone (m. p. 142–145°).

1,8-Diphenyl-*peri*-naphthindandione-7,9, as usually obtained, forms an orange crystalline powder that melts at 142–147°. After repeated crystallization from butyl alcohol, acetic acid or toluene, it may be obtained with a melting point of 152–154°.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.18; H, 4.63. Found: C, 86.05; H, 4.97.

The diketone forms a soluble red sodium salt, and it may be recovered unchanged after a suspension of this in 25% sodium hydroxide has been boiled for three hours. It is soluble in cold concentrated sulfuric acid, forming a brown solution, and in cold concentrated hydrochloric acid, forming an orange solution. The diketone is deposited unchanged when either of these solutions is diluted. Its solubility in acetic acid is greatly increased by the addition of a little concentrated mineral acid.

8-Phenylglyoxalyl-7(or 2)-phenyl-1-naphthoic Acid, IV.—By treating an alkaline solution of III (5 g.) with aqueous potassium permanganate (5 g.) below 10°, the diketo acid may be obtained in a yield of 50–60%. From acetic acid it separates as colorless prisms that melt at 199–200°. The compound is readily soluble in aqueous alkali, giving a bright yellow solution.

Anal. Calcd. for $C_{25}H_{16}O_4$: C, 78.9; H, 4.22. Found: C, 79.0; H, 4.25.

Attempts to obtain a methyl ether or a quinoxaline yielded only the unchanged substance. The diketo acid may be recovered unchanged after treatment with hot dilute alkali, but if it is heated with concentrated alkali, it is charred and in small part converted into V.

2-Phenylnaphthalic Anhydride, V.—This anhydride may be obtained from IV in good yield by the action of chromic acid in acetic acid at 60° or nearly quantitatively, together with benzoic acid, by the action of hydrogen peroxide on an alkaline solution of IV. By the action of chromic acid on diphenyl-*peri*-naphthindandione in acetic acid at 60°, the anhydride may be obtained directly in a yield of 35–40%. From acetic acid the substance separates in white crystals that melt at 239–240° and can be distilled unchanged in a vacuum.

Anal. Calcd. for $C_{18}H_{10}O_3$: C, 78.8; H, 3.68. Found: C, 78.7; H, 3.53.

Chrysoketone-10-carboxylic Acid, VI.—2-Phenylnaphthalic anhydride is sulfonated by sulfuric acid and is not affected by hot phosphorus oxychloride, but by boiling its solution in benzene with an excess of aluminum chloride it is converted quantitatively into the keto acid VI. This substance forms long orange needles from methanol that melt at 290–297° with gas evolution.

Anal. Calcd. for $C_{18}H_{10}O_3$: C, 78.8; H, 3.67. Found: C, 78.8; H, 3.63.

The methyl ester, prepared with methanol and sulfuric acid, forms orange prisms that melt at 164°.

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[3] Sodium acetate gives a poorer yield.

[4] *Cf.* Cesaris, *Gazz. chim. ital.*, **42**, II, 464 (1912).

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.2; H, 4.2. Found: C, 79.3; H, 4.1.

Distilled under reduced pressure, chrysoketone-10-carboxylic acid yields chrysoketone quantitatively. In agreement with the literature[5] this substance melts at 132.5° and gives an oxime that melts at 202°.

7-Methoxy-8-phenyl-*peri*-naphthindenone-9, VIII.—Methyl sulfate and 20% sodium hydroxide are added alternately to an alcoholic solution of 8-phenyl-*peri*-naphthindandione-7,9 until the further addition of alkali occasions no color change. The product, obtained in a good yield, crystallizes from acetic acid in large yellow prisms that melt at 117–118°.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9. Found: C, 83.9; H, 4.8.

1,8 - Diphenyl - 7 - methoxy - 1,9a - dihydro - *peri*-naphthindenone-9, IX.—To an ether solution of the methoxy ketone VIII (2.2 g.) is added enough of an excess of phenylmagnesium bromide to dissolve the precipitate first formed. The mixture is decomposed with iced hydrochloric acid, and the product, after purification by filtering its solution in alkali, crystallized from acetic acid. There is obtained 1.6 g. of the dihydro compound, tan needles that melt at 152°. The substance dissolves in aqueous alkali, forming a yellow-green fluorescent solution.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.7; H, 5.54. Found: C, 85.5; H, 5.80.

1,3-Dimethoxy-2,9-diphenyl-*peri*-naphthindene, X.—(a) Addition of methyl sulfate and alkali alternately to an alcoholic solution of the dihydro compound IX yields the dimethyl ether X; this separates from acetic acid as white needles that melt at 137°.

(b) Similar methylation of the dihydro compound II yields the same dimethyl ether X, which melts at 137° alone or mixed with that obtained under (a). Although white, the substance obtained from either source gives a delicate yellow-green solution in methanol.

Anal. (Product from II) Calcd. for $C_{27}H_{22}O_2$: C, 85.68; H, 5.86. Found: C, 85.69; H, 6.21.

1,8-Diphenyl-7-methoxy-*peri*-naphthindenone-9, XI.—(a) When phenyl-lithium is used in place of phenylmagnesium bromide for the phenylation of VIII, the dihydro compound IX cannot be obtained, but instead only the dehydrogenated substance XI can be isolated, and this in a yield of 20%.

(b) An alcoholic solution of the dihydro compound IX is treated with an excess of benzoquinone. The dehydrogenation product XI is deposited rapidly as a yellow powder that melts at 250–251°. Recrystallization from acetic acid or from toluene–ligroin gives orange plates that also melt at 250–251°.

(c) See the following section under compound XII.

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.2; H, 5.0. Found: C, 86.4; H, 5.3.

On boiling the methoxy ketone XI (0.1 g.) with acetic acid (5 ml.) and 40% aqueous hydrobromic acid (1.5 ml.) for ninety minutes it is converted quantitatively into 1,8-diphenyl-*peri*-naphthindandione-7,9, III, which melts at 146–147° alone or mixed with an authentic sample.

6,8-Diphenyl-7-methoxy-*peri*-naphthindenone-9, XII.—Treatment of the diketone III with alkali and methyl sulfate in the usual way gives a good yield of a mixture of alkali insoluble substances. By fractional crystallization from acetic acid, the mixture can be separated into the methoxy ketone XI which melts at 250–251° (mixed melting point) and the isomeric methoxy ketone XII. From methyl alcohol the latter substance is obtained in the form of yellow needles that melt at 141–142°.

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.2; H, 5.0. Found: C, 85.9; H, 5.1.

Like its isomer XI, this compound is cleaved by acetic acid and hydrobromic acid to the diketone III of melting point 146–147°, and thus neither of the methylation products can be a C methyl derivative.

Summary

A number of naphthindene derivatives and some of their more important reactions are described. The action of phenyl-lithium on 8-phenyl-*peri*-naphthindandione-7,9 and that of phenylmagnesium bromide on 7-methoxy-8-phenyl-*peri*-naphthindenone-9 are shown to involve 1,4-addition of the organo-metallic compounds to the ketones.

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(5) Schaarschmidt, *Ber.*, **49**, 1444 (1916).