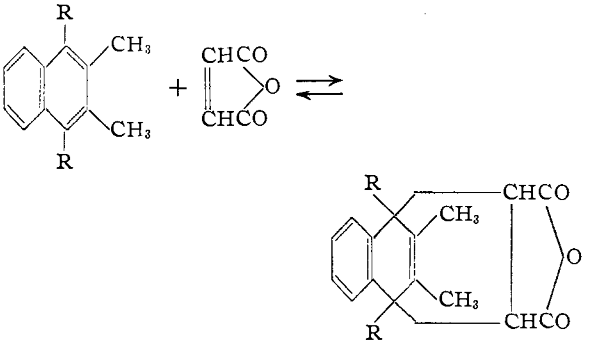
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

# Polymethyl Aromatic Hydrocarbons. IV. The Reaction of Alkylnaphthalenes with Maleic Anhydride[1]

BY MILTON C. KLOETZEL AND HERSHEL L. HERZOG[2]

We have recently demonstrated[3] a reversible Diels–Alder type reaction between maleic anhydride and 1,2,3,4-tetramethylnaphthalene, which yielded 1,2,3,4-tetramethyl-1,4-dihydronaphthalene-1,4-endo-$\alpha,\beta$-succinic anhydride (I).



I, R = $CH_3$
II, R = H

The realization of this reaction, under conditions which do not suffice to make naphthalene itself react significantly, was attributed to the activating influence of four methyl groups upon the potential diene system within the naphthalene nucleus.

It appeared of some significance to determine whether fewer methyl groups, or other alkyl groups, might not promote similar reactions of the naphthalene nucleus with maleic anhydride, and, if possible, to correlate the dienoid activity of the naphthalene nucleus with the extent and position of such substitution.

Adducts were indeed formed when 1,2,3,4-tetramethylnaphthalene, 1,2,4-trimethylnaphthalene, 1,2-, 1,4- and 2,3-dimethylnaphthalene, 2,3-diethylnaphthalene, and 2-methylnaphthalene were heated to 100° with a thirty-fold molar excess of maleic anhydride. 1-Methylnaphthalene and naphthalene itself also reacted under these conditions, but to a relatively insignificant extent. Adduct anhydrides were isolated by extraction of the reaction mixtures with water to remove excess maleic anhydride, followed by crystallization of the crude adducts from acetone or a mixture of ether and petroleum ether. Properties of these adduct anhydrides are summarized in Table I.

A more accurate determination of the extent of these Diels–Alder condensations was obtained by hydrolyzing the crude adducts with cold 5% potassium hydroxide, extracting the unreacted hydrocarbon, and weighing the adduct dicarboxylic acids which were liberated by acidification of the alkaline solutions. In Table II is shown the extent to which each hydrocarbon reacted with maleic anhydride during various periods of time. Yields were reproducible within 3.5%, as indicated by the results of duplicate determinations shown in Table II.

TABLE I

ADDUCTS FROM ALKYLNAPHTHALENES WITH MALEIC ANHYDRIDE

| Naphthalene | Cryst. form of adduct (solvent) | M. p. of adduct, °C. | Analyses of adduct, % Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|
| Naphthalene | Rods (ether) | 161–162 | 74.32 | 74.22 | 4.45 | 4.67 |
| 1-Methyl- | Prisms (ether–hexane) | 161–162 | 74.98 | 74.48 | 5.03 | 5.01 |
| 2-Methyl- | Prisms (hexane) | 138–139 | 74.98 | 74.68 | 5.03 | 5.05 |
| 1,2-Dimethyl- | Hex. prisms (acetone–p. e.) | 175.5–176 | 75.57 | 75.51 | 5.55 | 5.33 |
| 1,4-Dimethyl- | Prisms (ether) | 140–141 | 75.57 | 75.72 | 5.55 | 5.67 |
| 2,3-Dimethyl- | Prisms (acetone) | 177–178 | 75.57 | 75.68 | 5.55 | 5.71 |
| 1,2,4-Trimethyl- | Leaflets (ether–p. e.) | 159–160 | 76.10 | 76.25 | 6.01 | 6.14 |
| 2,3-Diethyl- | Prisms (acetone) | 177.5–178 | 76.57 | 76.88 | 6.43 | 6.20 |

TABLE II

EXTENT (%) OF REACTION OF ALKYLNAPHTHALENES WITH THIRTY MOLES OF MALEIC ANHYDRIDE AT 100°

| Naphthalene | Reaction time 1 hr. | 3.5 hr. | 24 hr. | 48 hr. |
|---|---|---|---|---|
| Naphthalene | | | <1, <1 | |
| 1-Methyl- | | | <1 | |
| 2-Methyl- | | | 14 | 11, 13 |
| 1,2-Dimethyl- | 7.5 | 27 (70)[a] | 25, 26 | 25 |
| 1,4-Dimethyl- | | 6 | 12 | 11 |
| 2,3-Dimethyl- | 5, 5 (93)[a] | 14, 16 (76)[a] | 43 (54),[a] 46.5 | 39[b] |
| 1,2,4-Trimethyl- | | . | 19, 21 | 21 |
| 1,2,3,4-Tetramethyl- | 74 (24)[a] | 93 | | 88 |
| 2,3-Diethyl- | 9 (90)[a] | 25 (71)[a] | 41 | 38 |

[a] Per cent. of unreacted hydrocarbon recovered is shown in parentheses. [b] Reaction time, seventy-two hours.

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[1] Presented before the Division of Organic Chemistry, Atlantic City, September, 1949. Abstracted from the dissertation submitted by Hershel L. Herzog to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Standard Oil Company of California Graduate Fellow in Chemistry.

[3] Kloetzel, Dayton and Herzog, THIS JOURNAL, **72**, 273 (1950).

An alternate method for the preparation of the adducts shown in Table I consisted in dissolving the adduct dicarboxylic acids, isolated in the aforedescribed manner, in a small volume of acetyl chloride, with the aid of gentle heating, and diluting the resulting solution with twice its volume of hexane or petroleum ether (b. p. 30–60°). Crystalline anhydrides then separated in good yields when the solutions were cooled for several hours.

The reversible nature of the Diels–Alder reaction with alkylnaphthalenes, as with anthracene derivatives,[4] is clearly evident. Heating the mixture of reactants beyond twenty-four hours did not increase the yield of adduct in any instance, and the reactions in the case of 1,2-dimethylnaphthalene and 1,2,3,4-tetramethylnaphthalene had already reached equilibrium within three and one-half hours. Unreacted hydrocarbons were recovered completely enough in several instances to indicate the absence of significant side reactions (see Table II). Finally, representative adducts (from naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and 2,3-dimethylnaphthalene) were shown to be dissociable. A quantitative yield of the respective hydrocarbon was obtained when each adduct was heated to 150° for twenty-four hours.

Of the alkylnaphthalenes investigated, 1,2,3,4-tetramethylnaphthalene showed simultaneously the most rapid rate of reaction with maleic anhydride and the most favorable equilibrium for adduct production. It is evident that a β-methyl substituent promotes a more favorable equilibrium for adduct formation than does an α-methyl substituent. Indeed, the substitution of a single methyl group in the 2-position appears to be as effective in promoting reaction as the simultaneous substitution of two methyl groups in the 1- and 4-positions.

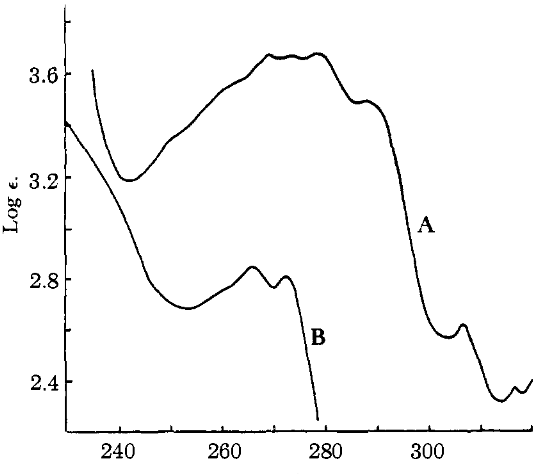

Fig. 1.—Absorption spectra: A, 2,3-dimethylnaphthalene; B, dipotassium 2,3-dimethyl-1,4-dihydronaphthalene-1,4-endo-α,β-succinate.

Although 2,3-dimethylnaphthalene and 2,3-diethylnaphthalene differ but little in their equilibrium yields of adducts, the latter hydrocarbon reacts somewhat more rapidly with maleic anhydride than does the former. This is of particular interest, for Bachmann and Chemerda[5] found ethyl groups in the 9- and 10-positions of 1,2-benzanthracene to have little activating effect compared to methyl groups in these same positions. Evidently the activating influence of an ethyl group is tempered by a hindering effect when the ethyl group is attached to the carbon atom at which the Diels–Alder addition occurs.

As a representative adduct, 2,3-dimethyl-1,4-dihydronaphthalene-1,4-endo-α,β-succinic anhydride (II) was subjected to a detailed examination. In Fig. 1 is shown the ultraviolet absorption curve for the adduct dipotassium salt in aqueous solution. Maxima, at approximately 266 and 272 mμ ($\epsilon_{\max}$ = 712 and 652, respectively) correspond closely with those shown by the anthracene-maleic anhydride adduct salt (at 266 and 274 mμ)[6] and by the 1,2,3,4-tetramethylnaphthalene adduct salt (at 265 and 272 mμ).[3] Beyond 275 mμ, absorption drops rapidly and decreases continuously as far as was measured to (340 mμ). These absorption characteristics indicate that the adduct is an alkylbenzene derivative and no longer contains an intact naphthalenic nucleus. For purposes of comparison, the absorption curve for 2,3-dimethylnaphthalene[7] is also shown in Fig. 1.

Hydrolysis of adduct II with potassium hydroxide appeared to be accompanied by partial isomerization, for the dibasic acid (III), precipitated by acidification of the aqueous solution of dibasic salt, melted over a varying range (171–178° for example) and was converted by means of diazomethane to a mixture of isomeric dimethyl esters (IV, m. p. 130–130.5° and 138–139°, respectively). Nor could the dibasic acid be successfully purified, for crystallization, even from the low-boiling solvents, caused partial reversion to the anhydride. Crystallization from solvents containing a small amount of acetic anhydride sufficed to make reversion complete.

Oxidation of the dicarboxylic acid (III) with alkaline potassium permanganate yielded phthalic acid (V), a clear indication that adduct formation involved the alkylated ring of 2,3-dimethylnaphthalene. The presence of an isolated double bond in the adduct was demonstrated by ozonolysis of the adduct dimethyl ester (IV, predominating isomer, m. p. 130–135.5°). Absorption of ozone at 0–5° was quantitative until approximately one mole had reacted, and hy-

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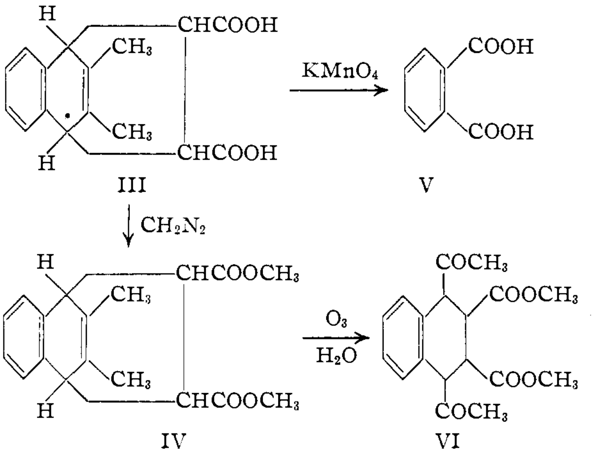
[4] Bachmann and Kloetzel, THIS JOURNAL, **60**, 481 (1938).

[5] Bachmann and Chemerda, *ibid.*, **60**, 1023 (1938).

[6] Clar, *Ber.*, **65**, 503 (1932).

[7] Compare Gavăt, Irimescu, Titeica and Vancov, *Chem. Abstr.*, **37**, 3670 (1943).

drolysis of the resulting ozonide produced a 40–50% yield of a substance which showed the proper analysis for dimethyl 1,4-diaceto-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (VI). Formation of a dioxime demonstrated the dicarbonyl character of this compound, and its failure to give a positive Schiff test or to reduce Fehling solution confirmed the presence of two keto groups.



Alkylnaphthalenes employed in this investigation were prepared essentially by methods already described in the literature. In some instances, however, modification of published methods resulted in better yields and/or purer products. Such modifications are described in the experimental part of this report.

**Acknowledgment.**—We wish to thank the Standard Oil Company of California for making this work possible through the financial aid provided by the Standard Oil Company of California Graduate Fellowship in Chemistry.

## Experimental[8]

**Alkylnaphthalenes.**—Twenty grams of 1-methyl-1-tetralol[9] was dehydrated by dissolving in 300 cc. of anhydrous formic acid and allowing the solution to stand for one hour at room temperature. Subsequent dilution with 600 cc. of water and extraction with ether yielded 15.9 g. of 1-methyl-3,4-dihydronaphthalene, b. p. 100° at 20 mm., which was dehydrogenated by heating to 270–300° for ten hours with 1.59 g. of palladium on barium sulfate catalyst.[10] The resulting oil was dissolved in methanol, filtered from catalyst, and the solution was added to a saturated solution of picric acid in methanol. Recrystallization of the precipitate from methanol yielded a picrate,[11] m. p. 140–141°, which was dissolved in benzene and extracted with 10% aqueous lithium hydroxide until the extracts were colorless. Evaporation of the benzene *in vacuo* left 10.0 g. of pure **1-methylnaphthalene**.

2-Methylnaphthalene (Reilly Tar and Chemical Corporation) was purified by conversion to the picrate, m. p. 114–115°, from which the hydrocarbon was recovered by the aforedescribed procedure.

**1,2-Dimethylnaphthalene, 1,4-dimethylnaphthalene** and **1,2,4-trimethylnaphthalene** were prepared by methods described by Kloetzel.[12] **1,2,3,4-Tetramethylnaphthalene** was prepared as described by Kloetzel, Dayton and Herzog.[3]

**2,3-Dimethylnaphthalene** was synthesized by modifying the general method employed by Barnett and Sanders[13] for the preparation of homologous naphthalenes. $\gamma$-(3,4-Dimethylphenyl)-*n*-butyric acid (88 g.) was dissolved in anhydrous hydrogen fluoride (800 g.) and the solution was allowed to stand for twelve hours at room temperature. The residual oil was washed with 10% sodium carbonate solution and distilled; yield, 70 g. (88%) of 6,7-dimethyl-1-tetralone, b. p. 125–130° at 2 mm. This ketone was reduced by the Clemmensen method[13] and the resulting 6,7-dimethyltetralin was dehydrogenated by heating to 290–300° with palladium on barium sulfate catalyst until hydrogen evolution ceased.

The absorption curve for 2,3-dimethylnaphthalene in 95% ethanol, shown in Fig. 1, was determined with a Beckman Quartz Spectrophotometer, Model DU.

**2,3-Diethylnaphthalene** was synthesized from tetralin in the following manner. To a mixture of 50 g. of tetralin, 38.6 g. of acetic anhydride and 200 cc. of dry, thiophene-free benzene, cooled in a Dry Ice-bath, was added 100 g. of anhydrous aluminum chloride. The reaction mixture was allowed to come to room temperature and was cooled when necessary to maintain a reaction temperature below 25°. After forty-eight hours, hydrolysis was effected with ice and hydrochloric acid, and 53 g. (74%) of 6-acetotetralin, b. p. 115° at 2 mm., was isolated in the customary fashion.[14]

6-Acetotetralin (53 g.) was refluxed for twenty-four hours with a mixture of 200 g. of amalgamated zinc, 200 cc. of concentrated hydrochloric acid, 300 cc. of methanol and 150 cc. of benzene. During the period of reflux, three additional 20-cc. portions of hydrochloric acid were added. Extraction of the mixture with benzene yielded 41 g. (84%) of 6-ethyltetralin,[15] b. p. 121–125° at 20 mm.

6-Ethyltetralin (30 g.) was acetylated as previously described for tetralin; yield, 29 g. (76%) of 6-aceto-7-ethyltetralin,[16] b. p. 125–130° at 1 mm. When this ketone was reduced as described for 6-acetotetralin, there was obtained an 87% yield of 6,7-diethyltetralin,[16] b. p. 141–146° at 20 mm.

When 10.0 g. of 6,7-diethyltetralin was heated to 290–310° for two and one-half hours with 0.5 g. of palladium on barium sulfate catalyst, 94% of the theoretical volume of hydrogen was evolved. The resulting **2,3-diethylnaphthalene** distilled at 165–170° at 20 mm.

2,3-Diethylnaphthalene picrate separated from methanol in orange needles, m. p. 127–127.5°. Arnold and Barnes[16] reported a m. p. of 126–128° for this picrate.

*Anal.* Calcd. for $C_{20}H_{19}O_7N_3$: C, 58.11; H, 4.63. Found: C, 58.15; H, 4.73.

The trinitrobenzene addition compound with 2,3-diethylnaphthalene separated from methanol in yellow needles, m. p. 127.5–128°.

*Anal.* Calcd. for $C_{20}H_{19}O_6N_3$: C, 60.45; H, 4.82. Found: C, 60.76; H, 4.85.

**Maleic Anhydride Adducts of Alkylnaphthalenes.**—A mixture of the alkylnaphthalene and thirty moles of freshly-distilled maleic anhydride was heated to 100° in a sealed tube for an appropriate period of time. The homogeneous solution was then poured into water (100 cc. per g. of hydrocarbon) and the mixture was stirred until all undissolved organic material rose to the surface. The residual

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[8] All m. p.'s are uncorrected. Analyses are by Dr. Adalbert Elek, Elek Micro Analytical Laboratories, Los Angeles, and by the Microanalytical Laboratory, California Institute of Technology, Pasadena.

[9] v. Auwers, *Ann.*, **415**, 98 (1918).

[10] Houben, "Die Methoden der organischen Chemie," 3rd ed., Verlag Georg Thieme, Leipzig, 1925, Vol. II, p. 500.

[11] v. Auwers, *Ber.*, **58**, 151 (1925), reported the picrate of 1 methylnaphthalene to melt at 142°.

[12] Kloetzel, THIS JOURNAL, **62**, 1708 (1940).

[13] Barnett and Sanders, *J. Chem. Soc.*, 434 (1933).

[14] Compare Scharwin, *Ber.*, **35**, 2511 (1902); Hesse, *ibid.*, **53**, 1645 (1920); Newman and Zahm, THIS JOURNAL, **65**, 1097 (1943).

[15] Compare Fleischer and Siefert, *Ber.*, **53**, 1255 (1920); Krollpfeiffer and Schaefer, *ibid.*, **56**, 620 (1923).

[16] Arnold and Barnes, THIS JOURNAL, **66**, 960 (1944).

mixture of adduct and unreacted hydrocarbon was separated from water by filtration (solids) or by a single extraction with ether (liquids or oily solids) and yielded the adduct anhydride (Table I) upon fractional crystallization from acetone or a mixture of ether and petroleum ether (b. p. 30–60°).

When the extent of the Diels–Alder reaction was to be determined quantitatively, the residual mixture of adduct and unreacted hydrocarbon was allowed to stand at room temperature for twenty-four hours with 5% aqueous potassium hydroxide (20 cc. per g. hydrocarbon employed).[17] Unreacted hydrocarbon was removed by filtration (solids) or extraction with ether (liquids) and the alkyl-1,4-dihydronaphthalene-1,4-endo-$\alpha,\beta$-succinic acid was precipitated by acidification of the alkaline solution with hydrochloric acid. The acidified solution was extracted once with a small quantity of ether in order to obtain any water-soluble dibasic acid, and the weight of dry residue, after spontaneous evaporation of the ether, was added to the weight of precipitated acid for calculation of the yield shown in Table II. The percentage of recovered unreacted hydrocarbon (shown in parentheses in Table II) indicated the absence of any significant side reaction.

Adduct dibasic acids were difficult to purify, for attempted recrystallization from even low-boiling organic solvents caused partial reversion to the corresponding anhydrides. This reversion could be made complete by dissolving the dibasic acid in the minimum volume of warm acetyl chloride. Dilution of the resulting solution with twice its volume of petroleum ether (b. p. 30–60°) and subsequent cooling for several hours in the refrigerator afforded a good yield of the corresponding crystalline alkyl-1,4-dihydronaphthalene-1,4-endo-$\alpha,\beta$-succinic anhydride. This procedure constituted an alternate method for preparation of the adducts described in Table I.

Representative adduct anhydrides (from naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and 2,3-dimethylnaphthalene) were shown to be dissociable. In a typical experiment, 0.10 g. of the adduct was heated to 150° in a sealed five-inch test-tube for twenty-four hours. Maleic anhydride and the alkylnaphthalene sublimed to the cooled part of the tube. To the mixture of dissociation products was added 2–3 cc. of water and one pellet of potassium hydroxide. Undissolved hydrocarbon was separated in substantially quantitative yield and was identified by means of a mixed m. p. determination with an authentic sample. In the case of the liquid 1-methylnaphthalene, the picrate was employed for mixed m. p. determination.

A sample of 2,3-dimethyl-1,4-dihydronaphthalene-1,4-endo-$\alpha,\beta$-succinic anhydride (II) was dissolved in the minimum volume of warm 5% aqueous potassium hydroxide, the solution was diluted to an appropriate volume with distilled water, and the absorption curve shown in Fig. 1 was determined in the customary manner.

**Oxidation of 2,3-Dimethyl-1,4-dihydronaphthalene-1,4-*endo*-$\alpha,\beta$-succinic Acid** (III).—To a solution of 500 mg. of III in 40 cc. of water containing 500 mg. of potassium carbonate was added, dropwise, 40 cc. of 5% potassium permanganate solution. The reaction mixture was swirled continuously and a temperature of 25° was maintained throughout the addition. Instant decolorization of the permanganate and simultaneous precipitation of manganese dioxide occurred until near the end of the addition. Finally, 1 cc. of ethanol was added and the mixture was warmed until complete decolorization had been achieved. Filtration with the aid of Norite yielded a colorless solution which was evaporated to a volume of 10 cc. and acidified with hydrochloric acid. Extraction of the acidic solution with several portions of ether separated 95 mg. of solid material which upon sublimation yielded 20 mg. of long, colorless needles, m. p. 130–131°. There was no depression of m. p. when this sublimate was mixed with authentic phthalic anhydride, m. p. 130–131°.

**Dimethyl 2,3-Dimethyl-1,4-dihydronaphthalene-1,4-*endo*-$\alpha,\beta$-succinate (IV).**—A 5.0-g. sample of adduct II was pulverized and warmed for five minutes with 100 cc. of 5% potassium hydroxide solution. Acidification of the resulting cooled solution with 10% hydrochloric acid caused the precipitation of 4.0 g. (75%) of the dibasic acid III, whose m. p. varied but was generally within the range 171–178°. An ethereal solution of diazomethane was added dropwise to an acetone solution of the dibasic acid until nitrogen evolution ceased and the yellow color of diazomethane persisted. Evaporation of the solvents left a crystalline residue, m. p. 105–110°, which, upon fractional crystallization from methanol, yielded two isomeric esters.

The more easily obtainable isomer separated from methanol in colorless massive prisms; yield, 2.0 g. (45%), m. p. 130–130.5°.

*Anal.* Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.78; H, 6.82.

Upon prolonged standing, mother liquors from crystallization of the first isomer deposited 1.1 g. (25%) of colorless, brittle, opaque needles (which required manual separation from prisms of the aforedescribed isomer), m. p. 138–139° after one additional recrystallization from methanol.

*Anal.* Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.86; H, 6.47.

A mixture of the two purified esters melted at 106–108°.

**Ozonolysis of Dimethyl 2,3-Dimethyl-1,4-dihydronaphthalene-1,4-*endo*-$\alpha,\beta$-succinate (IV).**—A stream of oxygen containing 3.4% ozone was passed through a solution of 1.0 g. (0.0033 mole) of ester IV (isomer melting at 130–130.5°) in 70 cc. of anhydrous ethyl acetate at the rate of 0.0087 mole of ozone per hour. The temperature of the solution was maintained at 0–5° and absorption of ozone was quantitative for twenty-five minutes. After treatment with the ozone stream for thirty-minutes, the solution of ozonide was poured into 25 cc. of water and the mixture allowed to stand for forty-eight hours. Separation of the layers, extraction of the aqueous layer with ether and subsequent evaporation of the combined organic layers at room temperature under reduced pressure yielded a gum, which finally crystallized upon standing in contact with a small amount of methanol. Recrystallization from methanol produced small rectangular prisms of dimethyl 1,4-diaceto-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (VI), m. p. 133.5–134°, in 40–50% yield.

*Anal.* Calcd. for $C_{18}H_{20}O_6$: C, 65.04; H, 6.07. Found: C, 65.15; H, 6.29.

This carbonyl compound did not give a positive Schiff test for aldehyde, nor did it reduce Fehling solution after boiling for several minutes and being allowed to stand for twelve hours.

A solution of 0.2 g. of diketone VI, 0.1 g. of hydroxylamine hydrochloride and 1 cc. of pyridine in 15 cc. of methanol was refluxed for one hour, the solution was concentrated by evaporation of solvents, diluted with 25 cc. of water and again evaporated to a small volume under reduced pressure. Crystalline rosettes separated upon standing for twelve hours. Recrystallization from water containing a few drops of methanol yielded the dioxime of VI, m. p. 180–183° dec.

*Anal.* Calcd. for $C_{18}H_{22}O_6N_2$: N, 7.73. Found: N, 7.47.

## Summary

It has been shown that naphthalene, 1- and 2-methylnaphthalene, 1,2-, 1,4- and 2,3-dimethylnaphthalene, 1,2,4-trimethylnaphthalene and 2,3-diethylnaphthalene react with maleic anhydride to form dissociable adducts. The equilibrium yields of adduct were determined for the reaction of five of these hydrocarbons with a thirty-fold

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[17] In order to insure complete hydrolysis of the 1,2,3,4-tetramethylnaphthalene adduct, it was necessary to shake a benzene solution of the crude adduct with 5% alkali for five hours.

molar excess of maleic anhydride at 100°, and were shown to vary from < 1% (for naphthalene) to 45% (for 2,3-dimethylnaphthalene).

The adduct from 2,3-dimethylnaphthalene and maleic anhydride was shown to be 2,3-dimethyl-1,4-dihydronaphthalene-1,4-endo-$\alpha,\beta$-succinic anhydride.

LOS ANGELES, CALIFORNIA RECEIVED OCTOBER 14, 1949

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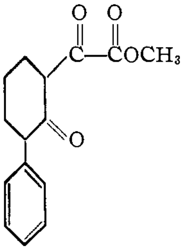
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# Reactions of 2-Arylcyclohexanones. I. Unsaturated Lactones Formed by Glyoxalation[1]

BY W. E. BACHMANN, G. I. FUJIMOTO[2] AND L. B. WICK[3]

An arylcyclohexane structure can be traced in such diverse structures as estrone and other steroids, morphine, and certain resin acids. An investigation of the chemistry of 2-arylcyclohexanones was initiated in order to determine their properties and their application to the synthesis of natural compounds or of useful analogs. At the time this study was begun little work had been done in this field. In the meantime a number of papers by other investigators on derivatives of these compounds have appeared.

From the reaction between 2-phenylcyclohexanone and dimethyl oxalate in the presence of sodium methoxide, a crystalline product was obtained which was not the expected glyoxalate I but a cyclic compound, the analysis of which corresponded to a structure formed from the glyoxalate by loss of the elements of methanol. The same product was obtained when diethyl oxalate was employed. The structure proposed for the product is the $\gamma$-lactone of 2-hydroxy-3-phenyl-2-cyclohexeneglyoxalic acid (II), which can also exist in the enolic form IIIa. Indeed, the enolic properties of the compound, solubility in aqueous alkali, production of a deep color with ferric chloride, and formation of ethers (IIIb and IIIc) and an ester (IIId), suggested the structure (II $\rightleftarrows$ IIIa) and excluded from consideration structures IV (an enolic structure would violate Bredt's rule[4]) and V (for which no enolic structure can be written).



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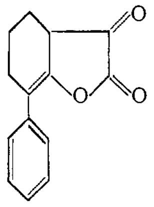

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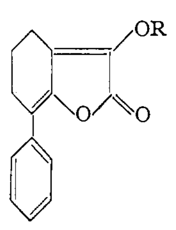
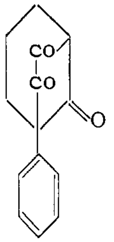
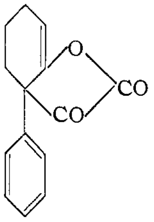


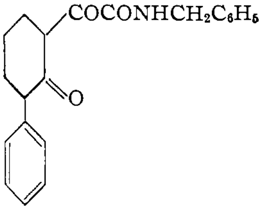
IIIa, R = H
IIIb, R = $CH_3$
IIIc, R = $C_2H_5$
IIId, R = $COCH_3$



IV



V



VI

The enol methyl ether (IIIb) was formed by reaction of the unsaturated lactone with diazomethane or with methanol in the presence of hydrogen chloride; the enol ethyl ether (IIIc) was obtained with ethanol and hydrogen chloride. The enol acetate (IIId) was produced when the lactone was treated with acetic anhydride. The enol ethers and ester gave no color with ferric chloride. Attempts to obtain the glyoxalic acid by opening the lactone ring with alkali were unsuccessful. Mild alkaline treatment simply gave the sodium enolate, a slightly soluble salt; more drastic treatment clipped off the oxalyl grouping and yielded 2-phenylcyclohexanone in 80% yield. The enol methyl ether IIIb also was cleaved by hot strong alkali to 2-phenylcyclohexanone in high yield; this result indicated that the compound was not a C-methyl derivative of IV. Benzylamine apparently opened the lactone ring, for it gave a compound which agreed with the benzylamide of the glyoxalic acid (VI) in analysis, was soluble in alkali, and gave an intense color with ferric chloride.

2-(*p*-Anisyl)-cyclohexanone, 2-(*m*-anisyl)-cyclohexanone and 2-(*p*-isopropyl)-cyclohexanone likewise yielded unsaturated lactones (VII) on gly-

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[1] Presented in part at the Chicago meeting of the American Chemical Society, April, 1948. The material is from the Ph.D. dissertations of G. I. Fujimoto and L. B. Wick.

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[4] Compare Bartlett and Woods, THIS JOURNAL, **62**, 2933 (1940).