< 40°, picrate m.p. 123° (phenyl 2-pyridyl ketone picrate[5] m.p. 128–129°). To the mixture was added an additional quantity of magnesium and magnesium iodide (prepared from 5 g. of magnesium and 14 g. of iodine) and on shaking, the yellow precipitate changed to a green precipitate. The mixture was refluxed on a water bath for 4 hr. and then allowed to stand at room temperature for 1 week after which time no visible change had taken place. The mixture was added to water and the benzene–ether layer separated. The water layer was washed several times with ether and the benzene–ether solution combined with the ether washings and dried over magnesium sulfate. Distillation of the solution yielded an orange oily solid which on washing with ethanol yielded 7.0 g. (38%), m.p. 139–140°, of white solid. The filtrate on evaporation yielded 4.3 g. of phenyl 2-pyridyl ketone. The white solid was recrystallized twice from ethyl acetate to constant m.p. 141–142° (lit.[3,6] m.p. 129–130°).

Anal. Calcd. for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47. Found: C, 78.40; H, 5.39.

Acknowledgment.—The authors thank Dr. Jerrold Meinwald for a critical discussion of this manuscript.

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[5] P. C. Teague, *J. Am. Chem. Soc.*, **69**, 714 (1947).

[6] The different melting points can be attributed to purity or to steric differences since *dl* and *meso* forms are possible.

Ring Expansion and Electron Transfer in the Cleavage of 2,2′-Diphenyl-2,2′-biindan-1,1′,3,3′-tetrone with Base[1]

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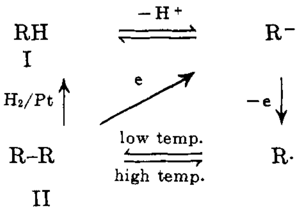
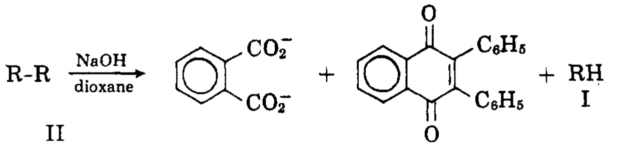
An article from this laboratory[3] reported the isolation of a dehydro dimer of 2-phenyl-1,3-indandione (I) as a minor product in the phenylation of I with diphenyliodonium chloride[4] or acetate[3] in *t*-butyl alcohol in the presence of sodium *t*-butoxide, the major product (85–93%) being 2,2-diphenyl-1,3-indandione. Although this dehydro dimer was obtained previously by other workers,[5] its mode of formation allowed formulations other than the proposed symmetrical C–C structure. New evidence[6] has confirmed the structure of this dehydro dimer as 2,2′-diphenyl-2,2′-biindan-1,1′,3,3′-tetrone (II). Also reported[6] were the synthesis of II by oxidation of 2-phenyl-1,3-indandione (I) in base, the homolytic and reductive cleavage of II, and its thermal rearrangement.[7]

The present work reports a new, heterolytic cleavage of II by sodium methoxide or sodium hydroxide and proposes a mechanism for the formation of the observed products.



Results.—Dehydro dimer II was cleaved to 2,3-diphenyl-1,4-naphthoquinone[8,9] (III, 76%), sodium phthalate, and 2-phenyl-1,3-indandione (I) when boiled with 1 *N* sodium hydroxide in dioxane. A hot methanolic solution of II containing sodium methoxide gave III, I, and methyl phthalate. The identity of the quinone III was proven by its melting point and infrared spectrum and by its conversion to 2,3-diphenylnaphthalene-1,4-diol diacetate[10] and to 2,3-epoxy-2,3-dihydro-2,3-diphenyl-1,4-naphthoquinone.[11]



II

III

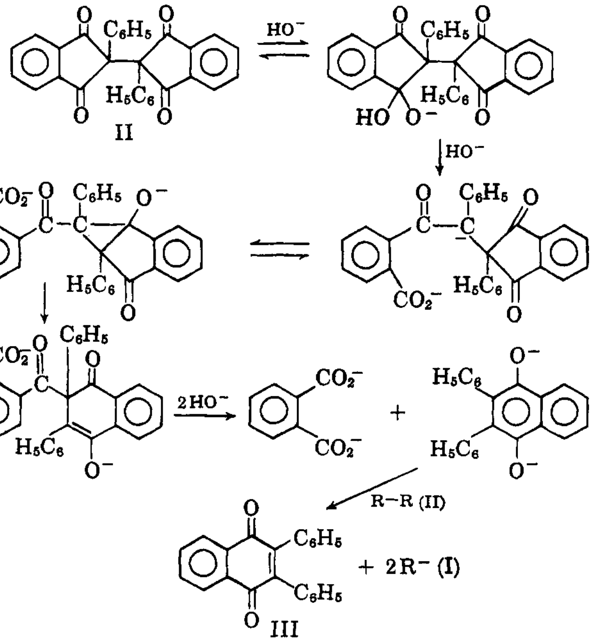
R = 2-phenyl-1,3-indandion-2-yl

While the sequence by which the dehydro dimer II is cleaved to give the 2,3-diphenyl-1,4-naphthoquinone and I is not fully established, it probably includes the formation of the dianion of the hydroquinone of III as an intermediate; indeed, 2,3-diphenylnaphthalene-1,4-diol[8] was isolated from the reaction in small quantities.

Proposed Mechanism for Ring Expansion.—A possible formulation of the cleavage of II by hydroxide ion is shown in Scheme I; the cleavage with methoxide ion can be interpreted analogously.

SCHEME I

PROPOSED MECHANISM FOR THE ALKALINE CLEAVAGE OF 2,2′-DIPHENYL-2,2′-BIINDAN-1,1′,3,3′-TETRONE



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[1] This article is taken from the doctoral dissertation of Suzanne A. Galton, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry).

[2] Eastman Kodak Co. Fellow, 1961–1962; Texaco Co. Fellow, 1963.

[3] F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Am. Chem. Soc.*, **84**, 2919 (1962).

[4] F. M. Beringer, E. J. Geering, M. Mausner, and I. Kuntz, *J. Phys. Chem.*, **60**, 141 (1956).

[5] (a) F. Nathanson, *Ber.*, **26**, 2576 (1893); (b) D. Radulescu and F. Barbulescu, *Bull. soc. chim. Romania*, **20**, 29 (1938); *Chem. Zentr. I*, 1830 (1940).

[6] F. M. Beringer, S. A. Galton, and S. J. Huang, *Tetrahedron*, **19**, 809 (1963).

[7] The rearrangement was first reported by J. Rigaudy and P. Auburn, *Compt. rend.*, **254**, 2372 (1962).

[8] R. Weiss and K. Bloch, *Monatsh.*, **63**, 39 (1933).

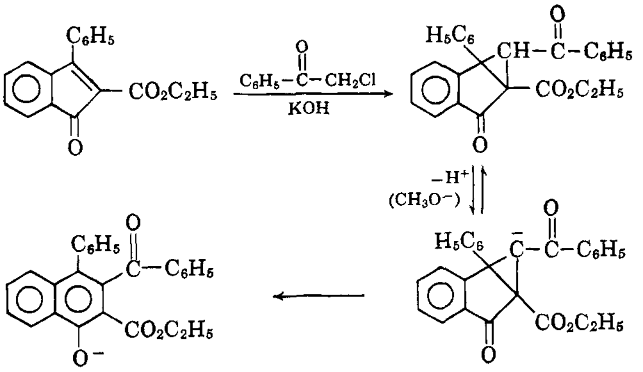
[9] H. M. Crawford, *J. Am. Chem. Soc.*, **70**, 1081 (1948).

[10] C. F. H. Allen, A. Bell, J. H. Clark, and J. E. Jones, *ibid.*, **66**, 1617 (1944).

[11] M. M. Shemyakin, D. A. Bochvar, and L. A. Shchukina, *J. Gen. Chem. USSR* (Eng. Transl.), **22**, 505 (1952); *Chem. Abstr.*, **47**, 2741*f* (1953).

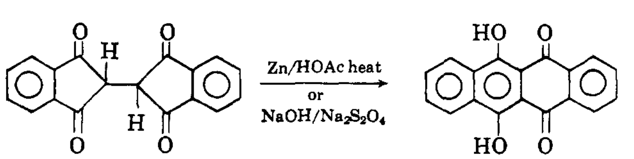
SCHEME II

AROMATIZATION OF A BENZO[3.1.0]BICYCLOHEXENONE (KOELSCH[12])



A related formation of a hydroxynaphthalene from a [3.1.0]bicyclohexanone under similar conditions was recently reported by Koelsch[12] and is formulated as Scheme II.

Another related ring expansion is that of 2,2′-biindan-1,1′3,3′-tetrone in the presence of zinc dust in acetic acid, or of sodium hydrosulfite (sodium dithionite) in aqueous alkali to form a dihydroxynaphthacenequinone.[13,14]



Reductive Cleavage of II.—The reductive cleavage of II to the anion of I has been effected by sodium in dioxane or liquid ammonia and by benzophenone ketyl.[6] It was also reported that in these reductions the quinone III was also formed in small amounts, possibly due to the presence of some hydroxide, alkoxide, or amide ions. In the present study the proposed reductive cleavage of II by the intermediate dianion of 2,3-diphenylnaphthalene-1,4-diol is supported by a separate experiment.

The quinone III was catalytically reduced to its hydroquinone, which in turn was converted to the dianion by sodium hydride in a dioxane solution. On addition of II to this solution and acidification, I (29%) was obtained along with unchanged II (61%). The dianion of the hydroquinone was easily reoxidized to III.

Experimental[15]

2,2′-Diphenyl-2,2′-biindan-1,1′,3,3′-tetrone (II).—The dehydro dimer II used in this study was prepared by oxidation of the anion of 2-phenyl-1,3- indandione (I) by iodine, according to the previously reported procedure.[6]

Cleavage of II by Aqueous Base.—A solution of 15.0 g. (34.0 mmoles) of II in 150 ml. of dioxane and 150 ml. of 1 *N* sodium hydroxide was refluxed overnight under nitrogen and then concentrated to about 50 ml. by distillation. A solution of the residue in 900 ml. of water was cooled in ice, and the yellow precipitate was collected. Extraction of the red filtrate with methylene chloride gave, on evaporation of the solvent, more yellow solid. The combined yield was 8.0 g. (25.7 mmoles, 76%) of impure **2,3-diphenyl-1,4-naphthoquinone** (**III**), m.p. 130–135°. The infrared spectrum of this impure quinone showed a hydroxyl band in the 3500-cm.$^{-1}$ region in addition to the expected[16] carbonyl band at 1665 cm.$^{-1}$.

When this impure quinone was dissolved in boiling ethanol, the small amount of colorless 2,3-diphenylnaphthalene-1,4-diol[17] which did not dissolve was collected, m.p. 200–224° (red melt); lit.[8] m.p. 236–243°, after softening at 220°.

It was not possible to remove this hydroquinone completely by recrystallization from ethanol. However, when oxygen was bubbled through a boiling solution of the mixture in ethanol for about 30 min., the color changed from a red-orange to a bright yellow and pure **2,3-diphenyl-1,4-naphthoquinone**, m.p. 140–141°, was isolated. Another recrystallization followed by sublimation at 140° (0.1 mm.) raised the melting point slightly, to 141–141.5°; lit.[9] m.p. 140–142°.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55; mol. wt., 310.3. Found: C, 85.00; H, 4.60; mol. wt., 318.

The ultraviolet spectrum had one band, $\lambda_{\max}^{\text{EtOH}}$ 250 mμ ($\epsilon_{\max}$ 27,000), and showed a broad shoulder with its maximum at 310 mμ.

The red aqueous phase from the cleavage was cooled, acidified, and filtered. The light tan solid was washed with water and dried to yield 2.0 g. (9 mmoles, 13%) of **2-phenyl-1,3-indandione**,[17] m.p. 145–147°; lit.[3] m.p. 149°.

The filtrate was further cooled to give as a white precipitate 2.88 g. (17.4 mmoles, 51%) of **phthalic acid**,[17] m.p. 204–205° dec.; lit.[18] m.p. 206–208° dec.

Cleavage of II with Sodium Methoxide.—To a solution of 4.6 g. (0.2 g.-atom) of sodium in 500 ml. of methanol, there was added with stirring 17.68 g. (40 mmoles) of II. The clear red solution was refluxed under nitrogen for 20 hr. and then concentrated to 50 ml. by distillation of the solvent. The residue was diluted with methylene chloride and extracted once with 0.1 *N* sodium hydroxide and twice with water. The red aqueous phase after acidification with hydrochloric acid, extraction with methylene chloride, and evaporation of the solvent, yielded a light orange crystalline residue. This on trituration with hexane–ether gave 5.56 g. (25 mmoles, 31%) of **2-phenyl-1,3-indandione** (I),[17] m.p. 141–143°.

The neutral yellow methylene chloride layer was concentrated to a thick oil, which was then dissolved in benzene and chromatographed on a 325-g. silica gel column. The column was eluted successively with hexane, benzene, methylene chloride, ether, and methanol. The benzene fraction on evaporation of the solvent and trituration of the residue with ether yielded 2.15 g. (4.85 mmoles, 12%) of II,[17] m.p. 210–213°. From the methylene chloride fraction 5.16 g. (16.6 mmoles, 41.5%) of **2,3-diphenyl-1,4-naphthoquinone** (**III**),[17] m.p. 139–140°, was isolated. One recrystallization from ethanol raised the melting point to 141–142°. The ether fraction on evaporation of the solvent gave 3.5 g. (18 mmoles, 45%) of **methyl phthalate**.[17]

When the reaction was run with one equivalent of sodium methoxide, 13% of I, 11% of II, 22% of III, and 38% of methyl phthalate were obtained.

2,3-Diphenylnaphthalene-1,4-diol and Its Diacetate.—When 200 mg. of 2,3-diphenyl-1,4-naphthoquinone was reduced under Clemmensen conditions (amalgamated zinc, concentrated hydrochloric acid, toluene), white shiny flakes formed in the toluene layer in 2 or 3 min. The white flakes were collected and recrystallized from benzene to yield 100 mg. of **2,3-diphenylnaphthalene-1,4-diol**, m.p. 205–225° (red melt); lit.[8] m.p. 236–243°, after softening at 220°.

The infrared spectrum of this compound was identical with that of the hydroquinone obtained in the previous reaction, showing a strong hydroxyl band at 3500 cm.$^{-1}$ and no carbonyl band at 1665 cm.$^{-1}$. No satisfactory analysis was obtained because of susceptibility to air oxidation. For this reason the acetoxy derivative was prepared.

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[12] C. F. Koelsch, *J. Org. Chem.*, **26**, 1003 (1961).

[13] (a) C. Dufraisse, *Bull. soc. chim. France*, [5] **3**, 1880 (1936); (b) G. Wanag, *Ber.*, **70**, 274 (1937).

[14] A. Schönberg and R. Moubasher, *J. Chem. Soc.*, 212 (1949).

[15] Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were taken on a Perkin-Elmer double beam recording spectrophotometer, Model 21, and a Perkin-Elmer Infracord spectrophotometer, Model 137. Ultraviolet spectra were taken on a Cary Model 11 recording spectrophotometer. Melting points were taken in capillary tubes and were corrected.

[16] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., J. Wiley and Sons, Inc., New York, N. Y., 1958.

[17] The infrared spectrum was superimposable on that of an authentic sample.

[18] "Handbook of Chemistry and Physics," 44th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1963.

To a solution of 1 g. of 2,3-diphenyl-1,4-naphthoquinone in 30 ml. of glacial acetic acid, 1 g. of powdered zinc and 5 ml. of concentrated hydrochloric acid were added. The mixture was boiled until the solution became colorless (5–10 min.) and a white solid separated. The mixture was then cooled, diluted with 200 ml. water, and extracted with methylene chloride. To the dried extract there were added immediately 1 ml. of pyridine and 1 ml. of acetyl chloride with cooling. The pale yellow solution was evaporated to dryness, and the residue was triturated with ethanol. The white crystals of **2,3-diphenylnaphthalene-1,4-diol diacetate** were collected and recrystallized from ethanol to yield 350 mg. of product, m.p. 199–200°, unchanged by further crystallization; lit.[10] m.p. 200–202°; ultraviolet spectrum: λ_{max}^{EtOH} 219 (ϵ 45,600) and 232 mμ (45,000).

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.69; H, 5.06.

2,3-Epoxy-2,3-dihydro-2,3-diphenyl-1,4-naphthoquinone.—To a hot solution of 1 g. (3.2 mmoles) of 2,3-diphenyl-1,4-naphthoquinone in 25 ml. of ethanol there were added 3 ml. of 30% hydrogen peroxide and 5 ml. of 10% aqueous sodium carbonate. The solution turned deep red and then colorless. After heating for 5 min., a solid separated. The mixture was cooled, diluted with 100 ml. of water and filtered. Two recrystallizations of the precipitate from ethanol yielded 720 mg. (2.2 mmoles, 69%) of **2,3-epoxy-2,3-dihydro-2,3-diphenyl-1,4-naphthoquinone,** m.p. 159–160°; lit.[11] m.p. 155–166°; ultraviolet spectrum: λ_{max}^{EtOH} 235 mμ (ϵ_{max} 37,200).

Anal. Calcd. for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32. Found: C, 81.08; H, 4.35.

Reductive Cleavage of II with the Dianion of 2,3-Diphenylnaphthalene-1,4-diol.—A solution of 1.0 g. (3.2 mmoles) of 2,3-diphenyl-1,4-naphthoquinone (III) in 50 ml. of dioxane was hydrogenated for 30 min. at 50 lb./in.[2] using 0.5 g. of platinum oxide as catalyst. After removal of the catalyst the solution was added to a suspension of 300 mg. (6.4 mmoles) of sodium hydride (51.6% in mineral oil) in 50 ml. of dioxane with stirring under nitrogen. After the evolution of gas ceased, a light brown-yellow solution was obtained. To this solution there was added with stirring a solution of 1.414 g. (3.2 mmoles) of II in 50 ml. of dioxane. The red solution was stirred at room temperature overnight and concentrated to a thick sirup. This was diluted with methylene chloride and extracted once with 0.1 *N* sodium hydroxide and once with water. The yellow organic phase was concentrated to a gum, which on trituration with methanol gave 1.88 g. of a yellow solid containing 0.87 g. (1.95 mmoles, 61%) of unchanged II and 1.0 g. (100%) of **2,3-diphenyl-1,4-naphthoquinone.** The concentrations of these two substances in the mixture were determined by ultraviolet spectroscopy from the optical density at 231 mμ of a solution in ethanol.

The red aqueous phase after acidification and extraction with methylene chloride gave 0.41 g. (1.84 mmoles, 29%) of **2-phenyl-1,3-indandione.**[17]

The Photochemical Conversion of Phenyl Isocyanate and Diphenyldiazomethane to 2,2-Diphenylindoxyl

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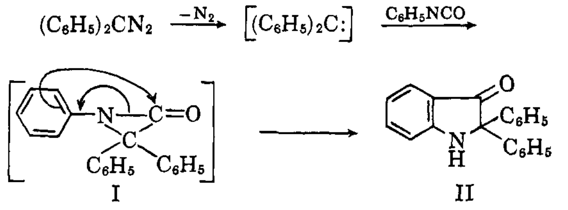
Received July 29, 1963

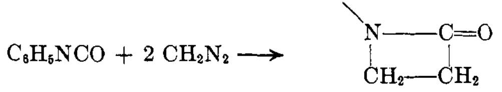
We have found that phenyl isocyanate and diphenyldiazomethane react under the influence of ultraviolet light to afford 2,2-diphenylindoxyl.[1] This reaction appears to be the first example of the addition of a carbene to an isocyanate and the first photoinitiated reaction of an isocyanate. In addition, each reactant is converted individually into a characteristic irradiation product; that is, diphenyldiazomethane produces benzophone azine[2] and phenyl isocyanate gives the cyclic dimer 1,3-diphenyluretedione.[3]

The formation of 2,2-diphenylindoxyl can be explained by assuming that the photo-generated carbene from diphenyldiazomethane adds to the phenyl isocyanate to produce an α-lactam I which then collapses to the indoxyl II.



Recently[1] this same α-lactam I was proposed as an intermediate in the reaction of α-chloro-α,α'-diphenylacetanilide with sodium hydride; in that case also 2,2-diphenylindoxyl (II) was the principal product.

In two earlier communications from this laboratory[4,5] the nonphotochemical reaction of diazomethane with phenyl isocyanate was reported to give a β-lactam (that of N-phenyl-β-alanine). At that time it was suggested[5] as one possible mechanism that first one molecule of diazomethane reacted with one molecule of phenyl isocyanate to give an intermediate α-lactam, which on subsequent reaction with a second molecule of diazomethane formed the β-lactam.



Staudinger stated[6] that diphenyldiazomethane does not react with phenyl isocyanate. Our present experiments confirm the absence of a detectable change on simple mixing of the reagents; heating decomposes diphenyldiazomethane to benzophenone azine. Irradiation, however, initiates a rapid reaction.

Experimental

Irradiation of Phenyl Isocyanate and Diphenyldiazomethane.—A solution of diphenyldiazomethane (1.2 g., 6.2 mmoles) in phenyl isocyanate (3.5 g., 29.6 mmoles) was irradiated[7] in a quartz tube with occasional cooling. After 6 hr. 115 ml. of nitrogen (25°) had been evolved and the deep violet color of diphenyldiazomethane had disappeared. The excess phenyl isocyanate was evaporated at room temperature and the residue was chromatographed over silicic acid (Mallinckrodt, 100 mesh). Elution with *n*-pentane–benzene yielded **benzophenone azine** (356 mg., m.p. 162–163°). Benzene eluted **1,3-diphenyluretedione** (53 mg., m.p. 174–175°); both were characterized by comparison with samples prepared by known methods.[2,3] Elution with benzene–ether (97:3) afforded 312 mg., m.p. 212–213° (after recrystallization from ether–petroleum ether), of **2,2-diphenylindoxyl.** Identification was made by mixture melting point and comparison of infrared and ultraviolet spectra with an authentic sample.[1] The molecular weight (mass spectrometric) was 285 (calcd. for $C_{20}H_{15}NO$: 285). Continued elution with benzene–ether gave a viscous red oil in which the probable pres-

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[1] J. C. Sheehan and J. W. Frankenfeld, *J. Am. Chem. Soc.*, **83**, 4792 (1961).

[2] T. Curtius and F. Rauterberg, *J. prakt. Chem.*, [2] **44**, 200 (1891).

[3] L. C. Raiford and H. B. Freyermuth, *J. Org. Chem.*, **8**, 230 (1943).

[4] J. C. Sheehan and P. T. Izzo, *J. Am. Chem. Soc.*, **70**, 1985 (1948).

[5] J. C. Sheehan and P. T. Izzo, *ibid.*, **71**, 4059 (1949).

[6] H. Staudinger, E. Anthes, and F. Pfenninger, *Ber.*, **49**, 1928 (1916).

[7] The irradiation was carried out from a distance of 12–15 cm. with a 140-w. Hanovia Utility Model high-pressure quartz mercury-vapor arc lamp, which transmits the complete ultraviolet spectrum.