155° gave 6.7 g. (32%) of a light oil, b.p. 60–66° (0.2 mm.), $n^{20}D$ 1.5443. Analysis by g.p.c. showed 11 peaks. Two peaks, retention times 52.5 and 61.0 min., respectively, made up 90–95% of the total. These were identified by internal comparison as 6-methyl-5-propyltetralin and 5-methyl-6-propyltetralin, respectively.

6-Methyl-5-propyltetralin.—A sample (2.0 g.) of 2-methyl-1-propylnaphthalene[6] was hydrogenated at 1100 p.s.i. and 130° in absolute ethanol over Raney nickel. After 12 hr. the hydrogen uptake had virtually ceased. The product was found to consist of two major components and eight minor components by g.p.c. analysis. The largest component, retention time 54.0 min., was purified by g.p.c. and the infrared spectrum showed strong absorption bands at 1600, 1500, and 810 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.30; H, 10.70. Found: C, 89.02; H, 10.62.

6-Propyltetralin.—Tetralin was converted to 6-propionyltetralin and the ketone reduced according to the procedure of Smith and Lo.[2] The 6-propyltetralin, b.p. 61–63° (0.3 mm.), was obtained in 54% yield over-all, and gave a single peak on g.p.c. analysis.

2-Propylnaphthalene.—A mixture of 15.5 g. of 6-propyltetralin and 0.8 g. of 5% palladium on charcoal was heated for 5 hr. at 300° while a slow stream of nitrogen was passed over the reaction mixture. The product isolated by distillation, b.p. 62° (0.1 mm.), was obtained in 80% yield. A boiling point of 130° (12 mm.) is reported.[7] The substance gave a single peak on g.p.c. analysis.

1-Chloromethyl-2-propylnaphthalene.—A mixture of 12 g. (0.07 mole) of 2-propylnaphthalene, 6.5 g. of paraformaldehyde, 18 g. of glacial acetic acid, 12 g. of 85% phosphoric acid, and 65 g. of concentrated hydrochloric acid was stirred vigorously while being heated for 5 hr. on a steam bath. The reaction mixture was diluted with water and extracted with ether. The product boiled at 98–100° (0.025 mm.), $n^{21}D$ 1.6053, 9.3 g. (60%).

Anal. Calcd. for $C_{14}H_{15}Cl$: C, 76.88; H, 6.91. Found: C, 77.17; H, 7.14.

1-Methyl-2-propylnaphthalene.—Nine grams (0.041 mole) of the previous chloromethylation product was treated with hydrogen at 34-p.s.i. initial pressure and 0.6 g. of palladium on charcoal in acetone. The product was isolated by distillation, b.p. 78° (0.3 mm.), $n^{25}D$ 1.5915, in 55–60% yield; lit.[8] $n^{25}D$ 1.5928.

5-Methyl-6-propyltetralin.—A solution containing 1.56 g. of 1-methyl-2-propylnaphthalene in 15 ml. of absolute ethanol was hydrogenated at 130° and 1050 p.s.i. over W-4 Raney nickel.[9] The product was isolated in the normal manner and g.p.c. analysis showed 10 peaks, the major one constituting about 66% of the total. The material responsible for this peak was isolated by repetitive g.p.c., and showed $\bar{\nu}$ 810 cm.$^{-1}$. The amount isolated was insufficient for analysis.

Gas Chromatography.—All the hydrocarbons were analyzed on a Model 154C Perkin-Elmer vapor fractometer using a 6 ft. × 0.25 in. 5% Ucon Polar on Chromosorb column at 200° with helium as carrier gas. The following retention times are representative though the actual times varied about ± 3% in various runs: 6-methyl-7-propyltetralin, 46 min.; 5-methyl-6-propyltetralin, 60 min.; 6-methyl-5-propyltetralin, 54 min.; 1-methyl-2-propylnaphthalene, 102 min. The 6-methyl-7-propionyltetralin was analyzed on an 8 ft. × 0.25 in. 5% Ucon Polar column at 220°.

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An Extention of the Gomberg–Bachmann Pinacol Synthesis

FRANK F. EBETINO[1] AND E. D. AMSTUTZ

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania

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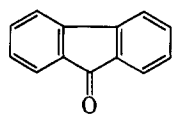
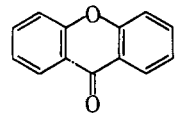
In 1927, Gomberg and Bachmann described the use of a magnesium–magnesium iodide mixture to reduce aromatic ketones to the corresponding pinacols.[2] This technique provided nearly quantitative yields, even in cases such as the reduction of fluorenone (I) and xanthone (II), where the corresponding pinacols

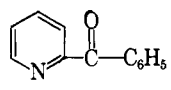


I

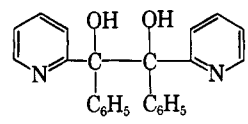


II

had not been obtainable by alternative methods. An apparent limitation of this reaction was noted, however, by Kegelman and Brown, who found that phenyl 2-, 3-, and 4-pyridyl ketones formed insoluble complexes with the magnesium halide.[3] These complexes gave only unchanged starting materials upon hydrolysis. In the case of phenyl 2-pyridyl ketone (III), a 14% yield of the desired pinacol, IV, was obtained by the use of sodium amalgam in aqueous alcohol. We wish to report the successful conversion of III to IV in better than twice this yield by a simple modification of the original Gomberg–Bachmann technique.



III



IV

In our initial investigations of this reduction, we obtained negative results similar to those of Kegelman and Brown. A yellow insoluble complex was formed which on hydrolysis yielded the original ketone. With an increased ratio of magnesium iodide to phenyl 2-pyridyl ketone, however, the yellow complex changed to a green precipitate which, on hydrolysis, gave a 38% yield of the pinacol IV.

The need for double the usual amount of magnesium iodide may be explained by assuming that the first half-mole serves to coordinate with the nitrogen of the pyridyl ketone, and that a second half-mole then serves to bring about the actual reduction.

Although we have not studied other examples of this reduction, it would appear that this simple expedient will allow the magnesium–magnesium iodide reductive dimerization to be applied to a wide variety of nitrogen-containing heterocyclic ketones.

Experimental[4]

α,α-Di-2-pyridylhydrobenzoin (IV).—To 5 g. of powdered magnesium (0.21 g.-atom) in 35 ml. of ether and 50 ml. of benzene was added with shaking 14 g. (0.055 mole) of iodine in portions to keep the solution boiling. After complete addition, the mixture was shaken until the liquid was practically colorless. To this mixture was added 18.3 g. (0.1 mole) of phenyl 2-pyridyl ketone dissolved in 30 ml. of benzene. A green precipitate separated which on shaking slowly turned to a yellow solid. The mixture was shaken and heated on a water bath for 1 hr., but no visible change occurred. A small portion of the mixture was withdrawn and hydrolyzed with water. The benzene–ether layer was dried and then evaporated to dryness to give a pale yellow solid, m.p.

(1) William S. Merrell Co. Fellow, 1951–1953; The Norwich Pharmacal Co., Norwich, N. Y.

(2) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **49**, 236 (1927).

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(4) Melting points are corrected.

< 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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(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]

F. MARSHALL BERINGER AND SUZANNE A. GALTON[2]

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn 1, New York

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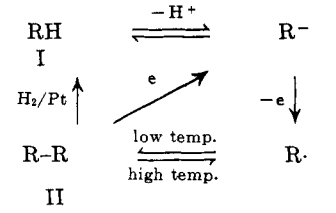
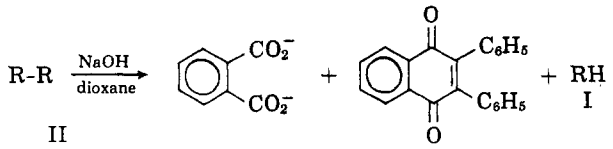
An article from this laboratory[3] reported the isolation of a dehydro dimer of 2-phenyl-1,3-indandione (I) as a minor product in the phenylation of I with diphenyliodonium chloride[4] or acetate[3] in *t*-butyl alcohol in the presence of sodium *t*-butoxide, the major product (85–93%) being 2,2-diphenyl-1,3-indandione. 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]



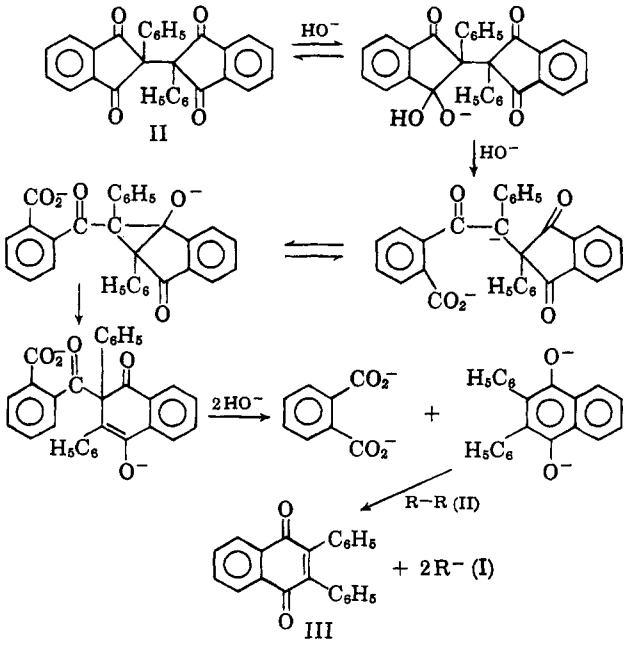
II R = 2-phenyl-1,3-indandion-2-yl III

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



(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.

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