Tetrahedron, 1963, Vol. 19, pp. 809 to 816. Pergamon Press Ltd. Printed in Northern Ireland

2,2′-DIPHENYL-2,2′-BIINDAN-1,1′,3,3′-TETRONE

A SYMMETRICAL ETHANE SUSCEPTIBLE TO HOMOLYTIC AND REDUCTIVE CLEAVAGE[1]

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(*Received* 12 *December* 1962)

Abstract—Oxidation of 2-phenyl-1,3-indandione (I) in base by the ferricyanide ion or by iodine gives the symmetrical C,C-dehydrodimer, 2,2′-diphenyl-2,2′-biindan-1,1′,3,3′-tetrone (II); an alternative formulation as the unsymmetrical O,C-dehydrodimer (III) is excluded. Dehydrodimer II is cleaved to I by catalytic hydrogenation at room temperature. Above 100° dehydrodimer II undergoes homolysis of the 2,2′-bond to form 2-phenyl-1,3-indandion-2-yl free radicals. These may abstract hydrogen from solvent (e.g. tetralin) or may recombine in a different manner: the 2-position of one radical adding to the *ortho*-position of the phenyl group of another radical. Tautomerism restoring the aromatic system of the phenyl group makes this addition irreversible and gives rearranged dehydrodimer (IV). Dehydrodimer II is cleaved by sodium to the anion of I.

INTRODUCTION

AS REPORTED earlier,[4] reaction of 2-phenyl-1,3-indandione[5] (I), with diphenyliodonium chloride[6] or acetate[4] in t-butyl alcohol containing sodium t-butoxide gave a high yield (85–93%) of the phenylated product, 2,2-diphenyl-1,3-indandione, and a small amount of a dehydrodimer to which the symmetrical structure II was tentatively assigned.[7] Alternative formulations (III–V) were not specifically excluded.

These formulas are to be considered not only because the various isomers have the appropriate composition and molecular weight but also because their origin is intelligible on the basis of the proposed mode of reaction of the diphenyliodonium ion with carbanions.[4] It has been proposed that electron transfer within iodonium ion–carbanion pairs ($Ar_2I^+R^-$) gives radical pairs ($Ar_2I{\cdot}R{\cdot}$ or $Ar{\cdot}R{\cdot}$). Most of these radical pairs react by coupling to ArR within their solvent cages. Diffusion apart, however, gives some free radicals, whose recombination can lead to ArR, ArAr and RR (or RR′).

Coupling of two R· radicals might be expected to occur at positions of greatest density of the odd electron. For the 2-phenyl-1,3-indandion-2-yl free radical these are the 2-position, the carbonyl oxygen and the *o*- and *p*- positions in the 2-phenyl group. Coupling between the 2-position of one radical and the 2-position, an oxygen or the *o*-position of another radical would give dehydrodimers II, III and IV respectively. The less likely formation of compound V would involve coupling between the 2-position of one radical and the 4- or 5- position (not substantially activated) of another.

The purpose of this research was to establish the structure of the dehydrodimer

[1] This article is taken from the dissertations of S. A. Galton and S. J. Huang, submitted for the degree of D. Phil. (Chemistry).
[2] Eastman Kodak Company Research Fellow, 1961–1962.
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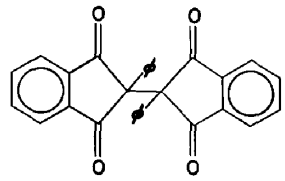
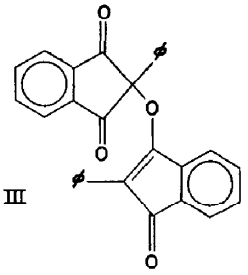
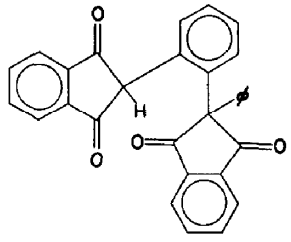
[4] F. M. Beringer, S. A. Galton and S. J. Huang, *J. Amer. Chem. Soc.* **84**, 2819 (1962).
[5] W. Dieckmann, *Ber. Dtsch. Chem. Ges.* **47**, 1439 (1914).
[6] F. M. Beringer, E. J. Geering, M. Mausner and I. Kuntz, *J. Phys. Chem.* **60**, 141 (1956).
[7] This structure was also assigned without cited experimental evidence to the dehydrodimer, m.p. 208°, obtained by treatment of 2-phenyl-1,3-indandione in ethanol with amyl nitrite: F. Nathanson, *Ber. Dtsch. Chem. Ges.* 26, 2576 (1893).



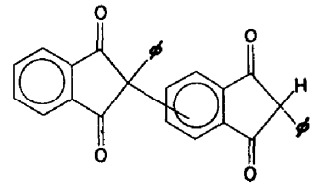
II



III



IV



V

formed as a minor product in the phenylation of 2-phenyl-1,3-indandione and to elucidate its surprising variety of reactions.

Structure of dehydrodimer. The dehydrodimer obtained from 2-phenyl-1,3-indandione is assigned structure II for the following reasons. (1) the dehydrodimer is transparent to visible light and to U.V. above 310 mμ; III should be yellow, as is 2-phenyl-3-methoxyindenone.[8] (2) The dehydrodimer shows in the I.R. spectrum no bands clearly ascribable to a vinyl ether (III) or to a trisubstituted benzene (V). (3) It is inert to bromine, permanganate, and hydrogen bromide in hot acetic acid; structures III–V suggest reactivity toward bromine, while III would react with permanganate and strong acid. (4) Brief treatment with cold aqueous base shows no reaction ascribable to an acidic hydrogen, as would be shown by IV and V.[9] (5) Reduction of the dehydrodimer with lithium aluminum hydride gives a tetrahydroxy compound, obtained crystalline in spite of the number of stereoisomers theoretically possible. That four equivalents of hydrogen were accepted by the dehydrodimer is shown by the analysis; that such reduction gave four hydroxyl groups is shown by the presence of an absorption band due to a hydroxyl group in the triacetyl derivative of the tetrahydroxy compound. This evidence rules out structure III. (6) Heating of the dehydrodimer in a tetralin solution gives 2-phenyl-1,3-indandione, as does catalytic hydrogenation. This behavior is understandable for II or III, as will be discussed below, but not for IV or V. Thus the weight of evidence favors structure II.

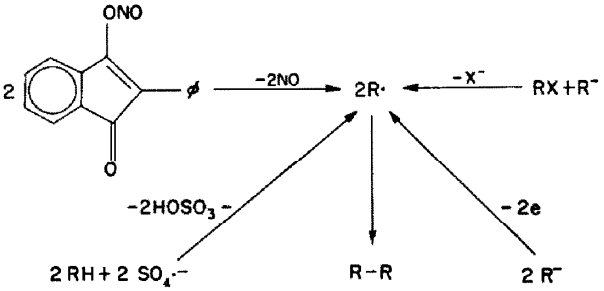
Coupling of 1,3-*indandiones.* Most if not all the conversions of 1,3-indandiones (RH) to dehydrodimers are reasonably formulated as involving formation of 1,3-indandion-2-yl free radicals (R·) and their coupling to 2,2′-biindan-1,1′,3,3′-tetrones (R-R). A standard method for abstracting hydrogen atoms is with free radicals from a peroxide; it has been reported that 2-methyl-1,3-indandione is converted to its dehydrodimer by potassium persulfate in hot water.[10] Free radicals are also formed by heating or

[8] A. Hantzsch and E. Czapp, *Z. physik. Chem.* Abt. A, **146**, 131 (1930).

[9] More vigorous treatment of II with base gives 2,3-diphenyl-1,4-naphthoquinone; a study of this reaction will be reported separately.

[10a] S. Gabriel and E. Leupold, *Ber Dtsch. Chem. Ges.* **31**, 1159 (1898); [b] A. Hantzsch and J. Lister *Liebig's Ann.* **392**, 319 (1912).

irradiation of alkyl nitrites.[11] Formation of II from 2-phenyl-1,3-indandione by treatment in ethanol with amyl nitrite[7] may involve transesterification to form an enol nitrite (RNO) and its decomposition to R· and nitric oxide. As suggested previously,[4] reaction of the carbanion R^- with the diphenyliodonium ion may yield R· by electron transfer.



In the present work it has been found that the coupling of 2-phenyl-1,3-indandione may be accomplished in high yield by treatment of its sodium salt with ferricyanide ion or with iodine. The former oxidation is clearly to be formulated as involving electron transfer, followed by coupling of two radicals. However, in the oxidative

$$R^- + Fe(CN)_6^{-3} \longrightarrow R\cdot + Fe(CN)_6^{-4}$$
$$2\,R\cdot \longrightarrow R{-}R$$

coupling by iodine present evidence does not allow a decision between the main mechanistic alternatives: electron transfer from carbon to iodine without formation of a carbon-iodine bond, and formation of 2-iodo-2-phenyl-1,3-indandione[12] (RI) as an intermediate.

$$2\,R^- + I_2 \longrightarrow 2\,R\cdot + 2\,I^-$$
$$RI + R^- + I^- \longrightarrow R{-}R + 2\,I^-$$

Hydrogenolysis of II. As steric and resonance factors should favor cleavage of the 2,2′-bond in dehydrodimer II (R—R), various methods of cleavage were attempted. It was first found that catalytic hydrogenation of II cleaved the 2,2′-bond, forming I in good yield. Here the heat of reaction of R—R with the catalyst may have supplied the energy for cleavage.

Homolysis of II. An attempt to effect the thermal homoylsis of II was successful: heating a solution of II in tetralin under reflux for one hour gave an 85% yield of I. It seems probable that the reaction proceeds by the homolysis of II, giving 2-phenyl-1,3-indandion-2-yl free radicals (R·), which then abstract hydrogen atoms from the α-positions of tetralin.

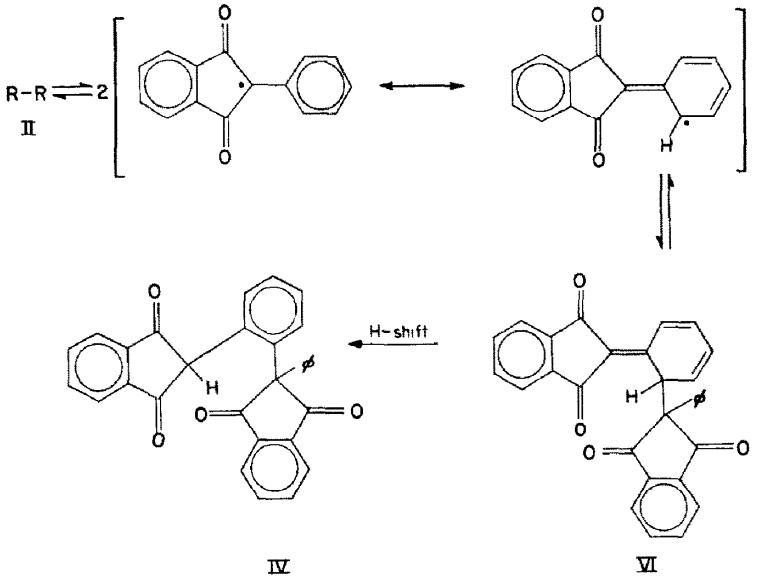
Rearrangement of II. In boiling cumene (isopropylbenzene, b.p. 152°) dehydrodimer II gave the product of homolysis (I) in only about 10% yield, while the main product (62·5%) was a higher-melting rearranged isomer. While work was in progress here to determine the structure of this product, a communication by Rigaudy and

[11] It is known that alkyl nitrites are decomposed by heat or light to nitric oxide and alkoxyl free radicals: P. Gray, P. Rathbone and A. Williams, *J. Chem. Soc.* 2620 (1961); D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *J. Amer. Chem. Soc.* **83**, 4076 (1961).

[12] While 2-iodo-2-phenyl-1,3-indandione is not known, the related bromo compound RBr has been reported and gives the dehydrodimer R—R on treatment with the carbanion R^-: D. Radulescu and F. Barbulescu, *Bul. Soc. Chim. Romania* **20**, 29 (1938); *Chem. Zent.* **1**, 1830 (1940).

Auburn[13] appeared in which it was reported that II on heating at its melting point (~213°) was converted to an isomer, m.p. 334–335°, of structure IV. Repetition of this work and comparison of the product with that obtained by heating in cumene showed the identity of the two products.

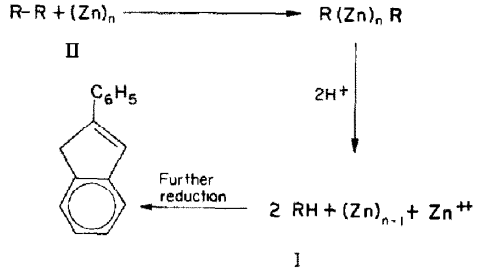
The rearrangement presumably occurs by homolysis of II to caged pairs of 2-phenyl-1,3-indandion-2-yl free radicals, some of which recombine to II, while some extract hydrogen from solvent. Others recombine in another way, forming VI. Compound VI may regenerate the same free radicals. However, a tautomeric shift in VI reestablishing the aromatic system in the phenyl group gives rearranged isomer IV (R—R′) irreversibly.



IV VI

The experimental results given above suggest that the energy of activation for hydrogen abstraction by R· from cumene or tetralin is greater than for the coupling of the two R· radicals.

Clemmensen reduction of II. Before the structure of dehydrodimer II had been established, it was felt that this structure might be supported and III (an enol ether) excluded by the Clemmensen reduction to yield a C_{30}-hydrocarbon. Reduction actually gave both a C_{15}-hydrocarbon (2-phenylindene) and a C_{30}-hydrocarbon. These results not only excluded structure III for the original dehydrodimer (II) but also

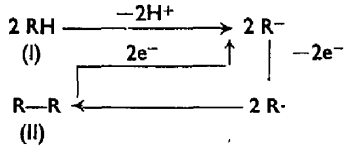


I

[13] J. Rigaudy and P. Auburn, *C.R. Acad. Sci. Paris* **254**, 2372 (1962).

showed that it might be cleaved reductively. If a cleavage product were 2-phenyl-1,3-indandione (I), then it should give 2-phenylindene; this has been shown to occur by the separate Clemmensen reduction of I.[14]

Reductive cleavage of II. The partial cleavage of II with amalgamated zinc and acid suggested that conditions might be found in which II would accept two electrons, with fission to two carbanions. Such a cleavage would be a reversal of the oxidative dimerization of I.



It was found that such a cleavage was effected by sodium metal, either suspended in dioxane or dissolved in liquid ammonia. Also, if sodium suspended in dioxane were treated with benzophenone to give the blue ketyl ($Na^+\phi_2\dot{C}—\bar{O}$), addition of a solution of II in dioxane discharged the blue color, replacing it with the red color of the anion of 2-phenyl-1,3-indandione.[15] Since this reductive cleavage occurs at temperatures below that of thermal cleavage of II, it is an example of electrolysis (in its original meaning) of the central bond of a 1,4-dicarbonyl compound.

Some years ago Löwenbein and Schuster[16] reported the behavior of a similar, dissociable ethane, 1,2-dibenzoyl-1,1,2,2-tetraphenylethane. That it gave free radicals in hot toluene is suggested by its reduction to benzoyldiphenylmethane by added phenylhydrazine. Sodium metal in hot toluene cleaved the ethane to give the anion of benzoyldiphenylmethane. While the authors explain this as homolysis to free radicals followed by reduction, the present results allow the alternative explanation of direct reductive cleavage of the ethane by sodium.

Reduction of II *without cleavage.* By the use of lithium aluminum hydride in ether the tetraketone II was reduced without cleavage to a tetrol, thus excluding alternative structure III. That a tetrol had indeed been formed was shown by conversion of the reduction product (presumably a mixture of diastereomers) to a triacetate which still contained a hydroxyl group (I.R. spectrum), as well as by reoxidation with chromic acid to the original tetraketone.

EXPERIMENTAL[17]

2,2′-Diphenyl-2,2′-biindan-1,1′,3,3′-tetrone (II)

While in the present work this compound was first encountered as a minor product from the reaction of 2-phenyl-1,3-indandione with diphenyliodonium chloride and sodium t-butoxide in t-butyl alcohol,[4] it was later prepared independently from 2-bromo-2-phenyl-1,3-indandione[7] and 2-phenyl-1,3-indandione by treatment with sodium ethoxide in ethanol.[18] Two more convenient syntheses follow.

[14] A study of the Clemmensen reduction of a series of mono- and diphenyl indanones and indandiones will be reported separately.

[15] An interesting minor product of such reactions was the yellow 2,3-diphenyl-1,4-naphthoquinone. The formation of this compound under the present conditions and others will be discussed in a separate report.

[16] A. Löwenbein and L. Schuster, *Liebig's Ann.* **481**, 106 (1930).

[17] Analyses were performed by Schwarzkopf Micro-analytical Laboratories, Woodside, N.Y. I.R. spectra were taken on a Perkin-Elmer double beam recording Spectrophotometer, Model 21, and a Perkin-Elmer Infrachord Spectrophotometer Model 137. U.V. spectra were taken on a Cary Model 11 recording Spectrophotometer. M.p.'s were taken in capillary tubes and were corrected.

To a solution of 4·94 g (225 mg atoms) of sodium in 600 ml ethanol there were added 49·5 g (225 mmoles) 2-phenyl-1,3-indandione and 25·5 g (113 mmoles) iodine. After the mixture had been stirred under reflux overnight, 450 ml solvent was removed by distillation. The crystals obtained from the chilled concentrate were thoroughly washed with 0·1N aqueous sodium thiosulfate, with water and with cold methanol and yielded after drying 45·0 g (102 mmoles, 91%) of colorless *2,2′-diphenyl-2,2′-biindan-1,1′,3,3′-tetrone* (II), m.p. 209–210°. Two recrystallizations from benzene–ethanol or benzene–hexane raised the m.p. to 213–214°, reported[7] m.p. 208°. (Found: C, 81·49; H, 4·22; M.W., 461; Calc. for $C_{30}H_{18}O_4$: C, 81·43; H, 4·10%; M.W., 442).

A solution of 12·4 g (56 mmoles) of 2-phenyl-1,3-indandione in 100 ml methylene chloride was stirred vigorously with a solution of 57 ml 1N NaOH in 100 ml water for 30 min. At the end of this time the aqueous layer had turned deep red, and the organic layer had become colorless. To this mixture there was added slowly a solution of 18·5 g (56 mmoles) potassium ferricyanide in 70 ml water. The aqueous phase turned orange at the end of the reaction. The mixture was stirred 5 min longer and the layers were separated. The aqueous layer was extracted with methylene chloride and the combined organic phases were extracted with 0·5N NaOH 3 times, to remove unchanged starting material, and once with water. After the organic phase had been dried ($MgSO_4$), the solvent was removed on a steam bath, and the oily residue triturated with ethanol. The white crystals were collected and dried in vacuum to yield 10·1 g (23 mmoles, 83%) *2,2′-diphenyl-2,2′-biindan-1,1′,3,3′-tetrone* (II), m.p. 194–200°; after 2 recrystallizations, m.p. 213–214°. The I.R. spectra of samples from all four sources were identical, as were the U.V. absorption maxima: λ_{max}^{EtOH} 231 mμ (ϵ_{max} 67,800).

At room temp this compound (II) did not react with bromine in carbon tetrachloride or with potassium permanganate in dioxane. It was also recovered unchanged after heating under reflux with 48% hydrobromic acid in acetic acid for 24 hr. It was not recovered, however, after solution in cold, conc sulfuric acid. While no observable reaction occurred on stirring with cold dilute aqueous sodium hydroxide, heating gave a mixture of cleavage products, as described separately.[15]

Hydrogenolysis of II

A solution of 5·0 g (11·3 mmoles) of the dehydrodimer II in 100 ml dioxane was hydrogenated over 5% platinum oxide on charcoal at 50 lb press. for 6 hr. After the catalyst had been removed, the orange solution was concentrated to dryness *in vacuo*. The residue was dissolved in methylene chloride and extracted with 1N NaOH. From the neutral organic phase 2·25 g (5·1 mmoles, 45%) of unchanged dimer was recovered. The red aqueous phase after acidification and extraction with methylene chloride yielded 2·15 g (9·7 mmoles, 43%) *2-phenyl-1,3-indandione*, m.p. 146–148°.

Thermal cleavage of II *in tetralin*

A solution of 1 g of the dehydrodimer II (2·26 mmoles) in 25 ml tetralin freshly distilled from sodium was refluxed under nitrogen. The colorless solution rapidly turned orange. After 1 hr the solution was cooled and extracted with 1N NaOH. The red aqueous phase was acidified with conc hydrochloric acid and extracted with methlyene chloride. The extract was concentrated to dryness and the residue was triturated with ether–hexane, to yield 850 mg (1·92 mmoles, 85%) *2-phenyl-1,3-indandione*, m.p. 142–144, reported[5] m.p. 149°.

Thermal rearrangement and cleavage of II

A solution of 2 g (4·5 mmoles) II in 50 ml freshly distilled cumene was heated under reflux overnight. Crystals in the chilled mixture were collected, washed with ether and dried to give 1·25 g (2·8 mmoles, 63%) crude IV, m.p. 290–300°. Recrystallization from tetralin raised the m.p. to 314–315°. (Found: C, 81·46; H, 4·20; Calc. for $C_{30}H_{18}O_4$: C, 81·43; H, 4·10%).

This material proved identical (m.p., mixed m.p., I.R. spectrum) to that prepared by heating II to its m.p. (~213°), according to the procedure of Rigaudy and Auburn,[18] who proved its structure to be IV, *2-phenyl-2-[o-(indan-1,3-dion-2-yl)-phenyl]-1,3-indandione*; they reported a m.p. of 334–335°

The cumene mother liquor from which IV had been filtered was diluted with benzene and extracted with aqueous sodium hydroxide. This extract on acidification gave 200 mg (0·9 mmole, 10%) *2-phenyl-1,3-indandione* (I), m.p. 145–146°.

Clemmensen reduction of II[18]

The amalgamated zinc was prepared by stirring 31 g granulated zinc and 3·1 g mercuric chloride

[18] A. Windaus and E. Rahlen, *Z. Physiol. Chem.* **101**, 223 (1918).

in 1·6 ml conc hydrochloric acid and 47 ml water for 5 min. The liquid was decanted, and to the zinc amalgam there was added 23 ml water, 70 ml toluene, 14·0 g (31·7 mmoles) of the dehydrodimer II and 55 ml conc hydrochloric acid. The mixture was stirred under reflux for 24 hr, during which period three 15 ml portions of conc hydrochloric acid were added. The mixture was cooled, and the yellow toluene layer was separated. The aqueous phase was extracted with ether, and the extract was combined with the toluene fraction. The combined extract was evaporated to dryness on a steambath, and the residue was chromatographed on a 500 g Florisil column (60/100 mesh) prepared in hexane. The column was eluted successively with hexane, benzene, methylene chloride, ether and methanol. From the hexane fraction 3·3 g (17·2 mmoles, 27%) yellow shiny flakes were obtained, which on recrystallization from hexane yielded 1·4 g (7·3 mmoles, 11·5%) white shiny flakes of 2-*phenylindene*, m.p. 166–167°. Sublimation at 100°/0·1 mm raised the m.p. to 167–168°, reported[18] m.p. 167·5°. (Found: C, 93·48; H, 6·22; mol wt, 179; Calc. for $C_{15}H_{12}$: C, 93·71; H, 6·29%; mol wt. 192.

The U.V. absorption spectrum showed the following bands, given as λ_{max}^{EtOH} (ϵ_{max}): 231 mμ (14,250), 238 mμ (13,950), 246 mμ (7,730), 302 mμ (25,300), 308 mμ (25,500) and 315 mμ (25,500); there is also a shoulder at 330 mμ.

Evaporation of the benzene eluate gave 6·7 g of an orange gum, which was triturated with ether to give 1·28 g of a yellow solid, m.p. 273–275°. Three crystallizations from chloroform gave pale yellow needles, m.p. 277–278°. (Found: C, 93·29, 93·23; H, 6·34, 6·78; mol wt. 384. Calc. for $C_{30}H_{36}$: C, 93·22; H, 6·78%; mol wt. 387).

Tests for olefinic unsaturation with bromine and with potassium permanganate in dioxane-water were negative, and it was recovered unchanged after catalytic hydrogenation over platinum in ethanol at room temp. Further discussion will be deferred until a later report.[14]

Reductive cleavage of II

(a) *Sodium in dioxane.*[20] A solution of 2·21 g (5 mmoles) of dehydrodimer II in 75 ml dioxane and 230 mg (10 mg atoms) sodium was refluxed under nitrogen for 6 hr. The solution turned dark red. The cooled solution was diluted to 500 ml with water and extracted 3 times with methylene chloride. The extract was evaporated to dryness, and the residue was triturated with ether to yield 100 mg pale yellow solid, whose IR spectrum showed that it was a mixture of unchanged dimer II and 2,3-diphenyl-1,4-naphthoquinone.[15]

The red aqueous phase was acidified with conc hydrochloric acid to yield 1·55 g (7 mmoles, 70%) of 2-*phenyl*-1,3-*indandione* (I).

(b) *Sodium in liquid ammonia.* To a suspension of 2 g (4·5 mmoles) of dehydrodimer II in 100 ml liquid ammonia was added 210 mg (9 mg atoms) sodium with good stirring. The mixture immediately turned orange-red, and after about 10 min no more change was observed. The ammonia was allowed to evaporate, and the residue was suspended in 200 ml water. The undissolved yellow solid was filtered, to yield 650 mg of a mixture of unchanged dimer and 2,3-diphenyl-1,4-naphthoquinone. Fractional crystallization from ethanol yielded about 100 mg (0·3 mmole, 7·2%) 2,3-*diphenyl*-1,4-*naphthoquinone*, m.p. 132–135°. The I.R. spectrum was identical to that obtained for the same compound isolated from the sodium hydroxide treatment of the dimer.[15]

The red aqueous filtrate was acidified with conc hydrochloric acid, and the precipitate was filtered to give 850 mg (3·8 mmoles, 43%) 2-*phenyl*-1,3-*indandione*, m.p. 139–145°.

(c) *Benzophenone ketyl in dioxane.* To a solution of 3·64 g (20 mmoles) of benzophenone in 50 ml dioxane there was added 460 mg (20 mg atoms) sodium with vigorous stirring. After the mixture had been boiled under reflux for about 15 min, the deep blue color of benzophenone ketyl began to appear. To the refluxing mixture there was then added dropwise a solution of 4·42 g (10 mmoles) dehydrodimer II in 75 ml dioxane. The addition was at such a rate that there was always an excess of blue color present in the reaction mixture; this required about 1 hr. The red solution was cooled and diluted to 500 ml with water. A yellow oil separated from the red solution, which was extracted with methylene chloride. The red aqueous phase on acidification and extraction with methylene chloride yielded 2·85 g (13 mmole, 65%) 2-*phenyl*-1,3-*indandione*, m.p. 144–147°.

[18] F. Mayer, A. Sieglitz and W. Ludwig, *Ber. Dtsch. Chem. Ges.* **54**, 1397 (1921).

[20] The dioxane used in this reaction was purified by passing 400 ml solvent through a 200 g neutral grade 1 alumina column, followed by distillation from sodium. The reaction was carried out in a nitrogen atmosphere.

The neutral methylene chloride extract on evaporation yielded a yellow oil which was chromatographed on a 200 g grade one neutral alumina column. The column was prepared in hexane and eluted successively with hexane, benzene, methylene chloride, ether, acetone and methanol. The first 3 fractions came through yellow from the column and were combined after evaporation of the solvent. The combined residue was dissolved in hexane, and the insoluble material was filtered, to yield 470 mg (10·6 mmoles, 10·6%) unchanged *dehydrodimer* II. The hexane solution was evaporated to a very small volume and allowed to crystallize to give 2·6 g of a yellow oily solid. Sublimation of this solid at 50–100°/0·1 mm gave 2·08 g (11·5 mmoles, 58%) *benzophenone*. The yellow glassy residue was triturated with ethanol to yield 440 mg of a yellow solid whose I.R. spectrum was identical to 2,3-*diphenyl*-1,4-*naphthoquinone* with a very small amount of dimer II as impurity.[15]

Reduction of II *to* 2,2′-*diphenyl*-2,2′-*biindan*-1,1′,3,3′-*tetrol without cleavage*

To a boiling suspension of 1·8 g (45 mmoles) lithium aluminum hydride in 250 ml anhydrous ether there was added 5 g (11·3 mmoles) II by extraction through a Soxhlet extractor over 3 days. The light gray mixture was cooled, and with stirring 10 ml conc sulfuric acid in 100 ml water was added dropwise. The yellow ether layer was separated immediately from the gray aqueous layer, dried ($MgSO_4$) and evaporated to dryness to yield 4·53 g pink-yellow solid. This solid was suspended in 50 ml boiling dioxane to remove the colored impurities. After cooling the white crystals were collected by suction filtration to give 3·2 g (7·1 mmoles, 63%) of 2,2′-*diphenyl*-2,2′-*biindan*-1,1′,3,3′-*tetrol*; m.p. 210–217° (turning orange at 170°). A small sample recrystallized twice from 1:1 pyridine–water on heating became orange at 170° and melted over a wide range to 220° (red melt). (Found: C, 80·14; H, 5·84; Calc. for $C_{30}H_{26}O_4$: C, 79·98; H, 5·82%).

The I.R. spectrum showed no carbonyl absorption but did have strong absorption at 3300 cm^{-1} (hydroxyl group). The U.V. absorption spectrum had the following bands, given as $\lambda_{max}^{n\text{-}BuOH}$ (ϵ_{max}): 260 mμ (1760), 267 mμ (2130), 273 mμ (1880).

Chromic acid oxidation of 2,2′-*diphenyl*-2,2′-*biindan*-1,1′,3,3′-*tetrol*

To a suspension of 200 mg 2,2′-diphenyl-2,2′-biindan-1,1′,3,3′-tetrol in 10 ml glacial acetic acid there was added dropwise a solution of 150 mg chromium trioxide in 10 ml glacial acetic acid, 1 ml conc sulfuric acid and 2 ml water. The solution turned dark green immediately and became homogeneous; the addition was continued until no further change occurred. The solution was poured over ice and water, and the precipitate was collected by suction filtration and dried, giving 250 mg solid; after trituration with ethanol, m.p. 210°–211°. The I.R. spectrum of this solid was identical to that of *dehydrodimer* II.

2,2′-*Diphenyl*-2,2′-*biindan*-1,1′,3,3′-*tetrol triacetate*

To a solution of 200 mg 2,2′-diphenyl-2,2′-biindan-1,1′,3,3′-tetrol in 5 ml pyridine there was added 5 ml acetic anhydride. The solution was heated at 100° for 1 hr and allowed to stand at room temp for 2 hr, then poured over 100 ml 3N HCl and ice. A gummy solid was collected and triturated with methanol. The resulting white solid was filtered and recrystallized from ethanol to yield 150 mg 2,2′-*diphenyl*-2,2′-*biindan*-1,1′,3,3′-*tetrol triacetate*, m.p. 194–195°. Two more recrystallizations did not raise the m.p. (Found: C, 74·80; H, 5·58; Calc. for $C_{36}H_{32}O_7$: C, 74·99; H, 5·59%).

The I.R. spectrum showed the presence of a hydroxyl band at 3500 cm^{-1}, a strong carbonyl absorption with a doublet at 1740 cm^{-1}, 1700 cm^{-1} and a strong C—O absorption with a doublet, possibly a triplet at 1200–1260 cm^{-1}.

The U.V. absorption spectrum showed the following bands, given as λ_{max}^{EtOH} (ϵ_{max}): 261 mμ (1210), 268 mμ (1450), 275 mμ (1170).