

## Epoxy Ketones. VII.<sup>1</sup> The Stereochemistry of Spiroepoxy Ketones. Reactions of 2-Benzal-1-indanone Oxide

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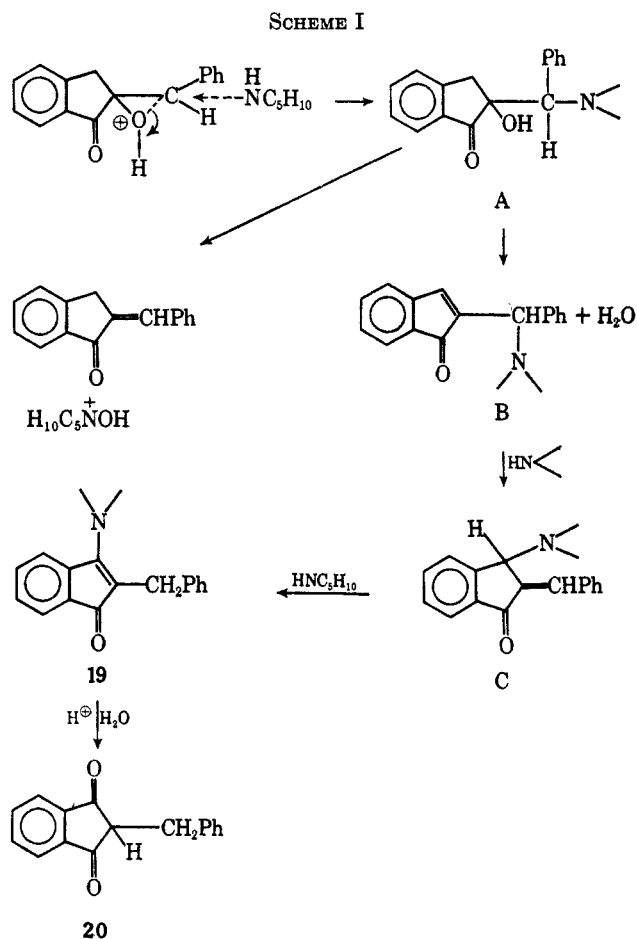
*trans*-2-Benzal-1-indanone epoxide (2a) resulted from a Darzens condensation of benzaldehyde with 2-bromoindanone (1). Spiroepoxy ketone 2a reacted with hydrogen chloride to give 2-( $\alpha$ -chlorobenzyl)-2-hydroxy-1-indanone (3) which reacted with morpholine to reproduce the epoxy ketone 2a. This epoxide ring is resistant to attack by amines but reacted with piperidine in the presence of sulfuric acid to give 2-benzyl-3-piperidino-1-indenone (19) along with 2-benzal-1-indanone. The spiroepoxy ketone 2a was converted into various hydroxy ketones, epoxy alcohols, and 1,2-diols by various hydrogenations or reactions with organometallic reagents. A study of the infrared spectra of these compounds provided for the assignment of their structures and configurations. The boron trifluoride rearrangement of the spiroepoxy ketone 2a gave enlargement to produce 2-phenyl-1,3-naphthandione (12). Hydrazine reacted with 2a to give a pyrazole 15, while the reaction with phenylhydrazine gave the three sequential products: the epoxy ketone phenylhydrazone 16, the hydroxypyrazoline 17, and the pyrazole 18.

Previous investigations in this series have included a study of the reactions of the spiroepoxy ketones, 2-benzal-1-tetralone oxides, with hydrogen chloride,<sup>1,3,4</sup> boron trifluoride,<sup>4</sup> chemical<sup>4</sup> and catalytic<sup>4</sup> reducing agents, organometallic reagents,<sup>4</sup> and phenylhydrazine.<sup>1,3</sup> These studies have now been extended to the analogous five-membered-ring ketone derivative, 2-benzal-1-indanone oxide (2), to determine the effect, if any, of the increased strain in the spiroepoxide ring.

*trans*-2-Benzal-1-indanone oxide 2a for these studies was prepared either by a Darzens-type condensation of 2-bromo-1-indanone (1) with benzaldehyde or by the base-catalyzed epoxidation of 2-benzal-1-indanone.<sup>5</sup>

The epoxide ring in the spiroepoxy ketone 2a was found to be very resistant to ring cleavage by morpholine or piperidine. It has been shown that the acyclic analog, *trans* chalcone oxide,<sup>6</sup> reacts readily with heterocyclic secondary amines by an S<sub>N</sub>2 attack at the  $\beta$ -carbon of the three-membered ring giving  $\beta$ -amino- $\alpha$ -hydroxy ketones. It appears that the  $\beta$ -carbon of the three-membered ring in 2a is sterically hindered to a backside attack by a nucleophilic reagent just as was found to be the case with 2-benzal-1-tetralone oxides.<sup>3</sup>

The acid-catalyzed reaction of 2a with piperidine led to two unexpected products, 2-benzal-1-indanone and 2-benzyl-3-piperidino-1-indenone (19),<sup>7</sup> in about a 1 to 2 ratio. The  $\beta$ -amino- $\alpha,\beta$ -unsaturated ketone 19 was readily hydrolyzed to the 1,3-diketone, 2-benzyl-1,3-indandione (20). The detailed course of these complex changes has not been established but a plausible one which would lead to the products isolated is outlined in Scheme I. The suggested decomposition of the proposed intermediate  $\beta$ -amino- $\alpha$ -hydroxy ketone A to produce 2-benzal-1-indanone is somewhat related to the amine oxide decompositions studied by Cope and his students.<sup>8</sup> 2-( $\alpha$ -Aminobenzyl)-1-indenones (B) are



known to rapidly undergo aminotropic rearrangements to give the isomeric amino ketones C, which are readily converted into the colored isomeric amino ketones 19 on heating with amines.<sup>7a,9</sup>

2a underwent three-membered-ring cleavage with gaseous hydrogen chloride in benzene solution to give the chlorohydrin whose structure was shown to be, 2-( $\alpha$ -chlorobenzyl)-2-hydroxy-1-indanone (3). Infrared absorption studies showed bands for both a hydrogen bonded ( $>C=O \cdots H-O-$ ) and nonbonded  $O-H$

(1) For paper VI, see N. H. Cromwell and R. E. Bambury, *J. Org. Chem.*, **26**, 1729 (1961).

(2) Abstracted from the Ph.D. Thesis of J. L. Martin, University of Nebraska, 1966.

(3) N. H. Cromwell, R. E. Bambury, and R. P. Barkley, *J. Amer. Chem. Soc.*, **81**, 4294 (1959).

(4) N. H. Cromwell and R. E. Bambury, *J. Org. Chem.*, **26**, 997 (1961).

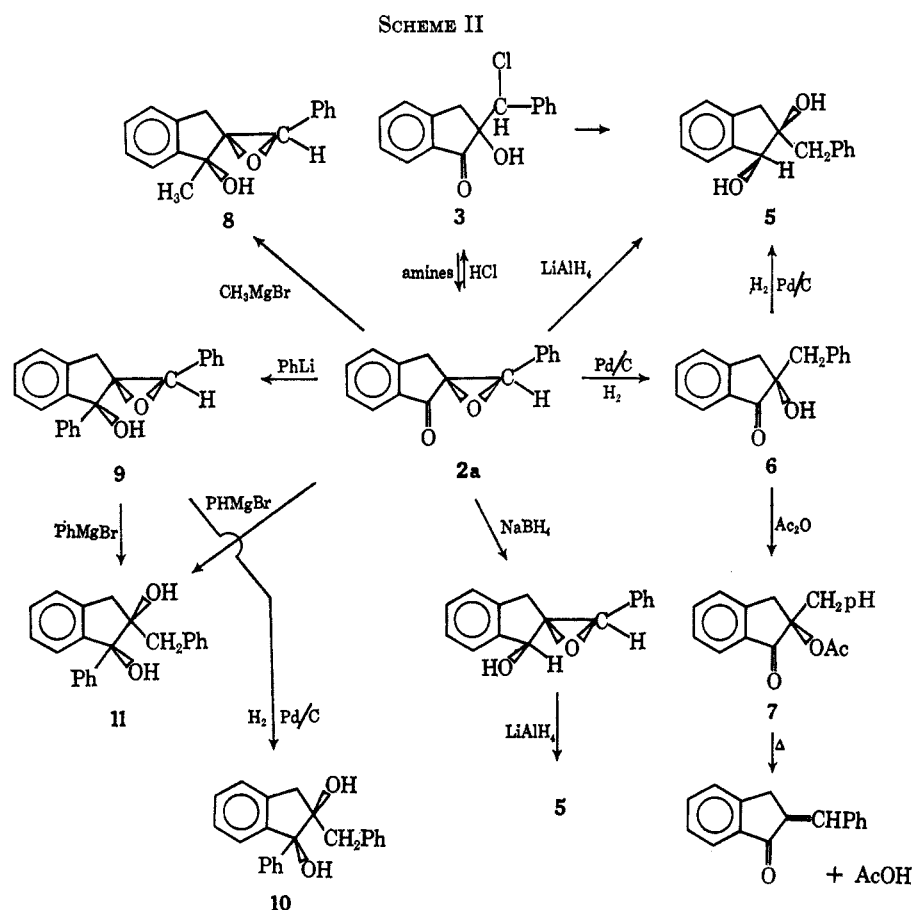
(5) A. Hassner and N. H. Cromwell, *J. Amer. Chem. Soc.*, **80**, 893 (1958).

(6) N. G. Barker and N. H. Cromwell, *ibid.*, **73**, 1051 (1951).

(7) (a) In an unpublished investigation (E.-M. Wu, Ph.D. Thesis, University of Nebraska, 1966) compound 19 has also been obtained by a base-catalyzed prototropic rearrangement of 2-benzal-3-piperidino-1-indanone (C). (b) see, B. D. Pearson, R. P. Ayer, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3038 (1962).

(8) See A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).

(9) (a) See H. H. Cromwell and E.-M. Wu, *Tetrahedron Lett.*, 1499 (1966). (b) 2-( $\alpha$ -Piperidinobenzyl)-1-indanone, prepared from 2-( $\alpha$ -chlorobenzyl)-1-indanone [D. N. Kevill, G. A. Coppens, M. Coppens, and N. H. Cromwell, *J. Org. Chem.*, **29**, 382 (1964)], is not rearranged to 19 on heating with excess piperidine in the presence of piperidine hydrochloride.



stretching vibration. The hydrogen bonding was shown to be intramolecular rather than intermolecular by dilution studies. Heating 3 with morpholine reproduced the *trans* epoxy ketone 2a. These results are comparable with those obtained with the 2-benzal-1-tetralone oxides.<sup>1,3,4</sup>

It was of interest to compare the stereochemistry of hydrogenation reactions (Scheme II) of epoxy ketone 2a to produce various epoxy alcohols and diols with comparable studies previously done with the 2-benzal-1-tetralone oxides.<sup>4</sup> The assignment of configurations to the diols resulting from these hydrogenations were readily made using an infrared absorption method previously developed by Kuhn<sup>10</sup> for the cyclopentadiols and which had been successful as applied by us to the assignment of configurations and conformations of the vicinal dihydroxy tetralins.<sup>4</sup>

The epoxy ketone 2a was reduced to 2-benzal-1-indanol oxide (4) in good yield with sodium borohydride in methanol solutions. Infrared studies showed a band at  $3620\text{ cm}^{-1}$  for a free secondary hydroxyl group<sup>10</sup> and another band of nearly equal intensity at  $3595\text{ cm}^{-1}$  which did not decrease on dilution. This latter band represented the vibration for the hydroxyl group internally hydrogen bonded to the epoxide oxygen, implying a *cis* arrangement for these groups.

The catalytic hydrogenation of the chlorohydrin 3 gave 2-benzyl-1,2-indandiol (5) which infrared absorption studies indicated had the vicinal hydroxyl groups *cis* to each other. The diol 5 of the same configuration resulted from the lithium aluminum hydride reduction

of both the epoxy alcohol 4 and the epoxy ketone 2a. Catalytic hydrogenation of the epoxy ketone 2a under carefully controlled conditions gave 2-benzal-2-hydroxyindanone (6) which on further catalytic hydrogenation gave the *cis*-diol 5. The ketol 6 reacted with acetic anhydride to give 2-acetoxy-2-benzyl-1-indanone (7) which was pyrolyzed to 2-benzal-1-indanone.

The addition of a methyl Grignard solution to an ether solution of the epoxy ketone 2a produced a good yield of 1-methyl-2-benzal-1-indanol oxide (8). The infrared absorption of 8 gave no indication of intramolecular hydrogen bonding; it was not possible to assign its configuration on this basis.

The epoxy ketone 2a added phenyllithium to the carbonyl group to give a good yield of 1-phenyl-2-benzal-1-indanol oxide (9). This result is similar with that previously reported by Bickel<sup>11</sup> for various acyclic epoxy ketones. The infrared absorption of this epoxy alcohol also showed only one band for a free tertiary hydroxyl group. Nevertheless, the configuration is shown to be as assigned on the basis of the catalytic hydrogenation of 9 to the *cis*-diol, 1-phenyl-2-benzyl-1,2-indandiol (10). The infrared absorption of the diol 10 showed a band at  $3605\text{ cm}^{-1}$  for the free tertiary hydroxyl groups and a less intense band at  $3570\text{ cm}^{-1}$  for the hydrogen bonded hydroxyl group, which did not fade in relative intensities on dilution.

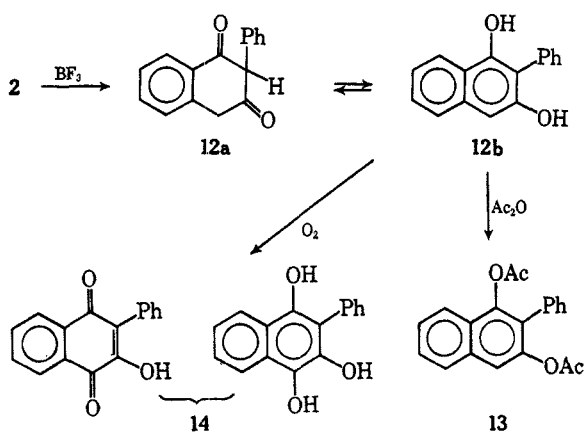
Treatment of the epoxy alcohol 9 with phenylmagnesium bromide produced another *cis*-diol, 1-phenyl-2-( $\alpha$ -phenylbenzyl)-1,2-indandiol (11), which was also obtained on treating the epoxy ketone 2a with the same reagent. The infrared absorption of the diol 11

(10) (a) L. P. Kuhn, *J. Amer. Chem. Soc.*, **74**, 2482 (1952); (b) L. P. Kuhn, *ibid.*, **76**, 4323 (1954).

(11) C. L. Bickel, *ibid.*, **59**, 325 (1937).

showed a free hydroxyl band at  $3601\text{ cm}^{-1}$  and an intramolecular hydrogen-bonded hydroxyl band at  $3556\text{ cm}^{-1}$ .

When the spiroepoxy ketone **2a** was heated with the Lewis acid, boron trifluoride, under the conditions described by House and Wasson for rearranging 2-benzalicyclopentanone oxide to 2-phenyl-1,3-cyclohexanedione<sup>12</sup> and applied by us<sup>4</sup> to rearrange 2-benzal-4,4-dimethyl-1-tetralone oxide to 6-phenyl-9,9-dimethyl-benzocycloheptane-5,7-dione, a good yield of 2-phenyl-1,3-naphthandione (**12**) was obtained. This known

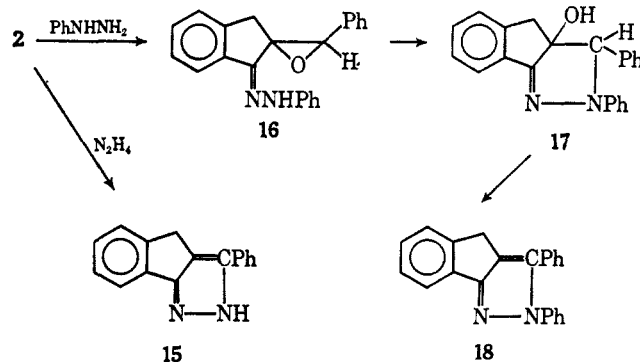


compound **12** has been studied by several groups<sup>13</sup> since it was first synthesized by Volhard<sup>13a</sup> by the reaction of  $\alpha,\gamma$ -diphenylacetoacetate with concentrated sulfuric acid. This product **12** showed infrared absorption at  $3602$  and  $3580\text{ cm}^{-1}$  in the hydroxyl stretching region and at  $1658$  and  $1647\text{ cm}^{-1}$  in the carbonyl stretching range of the spectrum. This is indicative of extensive enolization (form **12b** and probably monoenolic forms), which is analogous to the observation of House and Wasson<sup>12</sup> for 2-phenyl-1,3-cyclohexanedione. The nmr spectrum of **12** also gave evidence for enolization with a band at  $\tau$  0.53, integrating for 1.5 hydroxyl protons, and a band at 2.21, integrating for 1.5 methine (or aromatic) protons, with nine aromatic protons in a broad band at 2.83–3.75.

The diacetoxy derivative **13** was prepared and found to have the characteristics described by Volhard.<sup>13a</sup> An oxidation product, the quinhydrone **14**, had the properties previously<sup>13a,c,d</sup> described for the substance. The nmr spectrum of the substance **14** agreed well for the quinhydrone structure.

The reaction of various epoxy ketones with hydrazines has been found to give hydroxypyrazolines as first products, in some cases, which were then readily dehydrated to pyrazoles.<sup>1,3,14–16</sup> The only isolable product from the reaction of 2-benzal-1-indanone with hydrazine hydrate was 5-phenyl-3,4-indano( $\Delta^{2,4}$ -pyrazole) (**15**).<sup>17</sup> The reaction of 2-benzal-1-indanone oxide with phenylhydrazine produced a mixture of three products which were separated by chromato-

graphy on an alumina-packed column. These products were shown to be the sequential epoxyphenylhydrazone **16**,<sup>17</sup> the hydroxypyrazoline **17**,<sup>17,18</sup> and the



pyrazole **18**;<sup>17</sup> compound **18** showed an ultraviolet absorption spectrum similar to that of **15** and other pyrazoles.<sup>1,3,17</sup> The nmr spectra of **16**, **17**, and **18** were consistent with the structures assigned to these products.

It may be concluded that the reactions of 2-benzal-1-indanone oxide (**2a**) are closely related to those experienced with 2-benzal-1-tetralone oxide.<sup>1,3</sup> In the former the cyclization of the first-formed phenylhydrazone **16** to the hydroxypyrazoline **17** is slow enough, as is the dehydration of **17** to the pyrazole **15**, to allow the isolation of the intermediate products. This was not the case for the reaction of 2-benzal-1-tetralone oxide with phenylhydrazine.

### Experimental Section<sup>19</sup>

**2-Bromo-1-indanone (1)** was prepared in 91% yield by the published method;<sup>20</sup> mp  $36\text{--}37^\circ$ ; infrared absorption<sup>19</sup> at  $1727$  ( $\text{C}=\text{O}$ ); and nmr peaks at 2.1–2.7 (for aromatic protons), at 5.31–5.55 (a one-proton quartet), and at 6.5 (a two-proton doublet).

**2-Benzal-1-indanone oxide (2).**—This known compound (**2**) was prepared by a Darzens-type condensation of 1.05 g (0.005 mol) of bromo ketone **1** with 0.53 g (0.005 mol) of benzaldehyde in 9 ml of a mixture (2:1) of methanol and dioxane. The solution was cooled in an ice-salt bath and 0.11 g (0.005 mol) of sodium dissolved in 2 ml of methanol was added dropwise with stirring over a period of 30 min. After 1 hr a solid appeared. The solution was stirred an additional hour and then neutralized with dilute acetic acid to precipitate 1.01 g (86.5% yield) of nearly pure product, mp  $118\text{--}121^\circ$ , identical with an authentic sample.<sup>5</sup> This appeared to be the nearly pure *trans* isomer **2a**; see below.

Compound **2** was also prepared many times by the base-catalyzed epoxidation of 2-benzal-1-indanone.<sup>5</sup> In spite of attempts to ensure identical conditions varied results were obtained from one run to the next. Often the product possessed a broad melting point,  $114\text{--}121^\circ$ . In one run a small amount of the lower melting isomer **2b**, mp  $114\text{--}115^\circ$ , was isolated. On allowing this sample to solidify it was again found to remelt at  $114\text{--}116^\circ$ . The nmr

(18) See N. H. Cromwell, *et al.*, *ibid.*, **73**, 1044 (1951), for ultraviolet spectra of other pyrazolines.

(19) All melting points are corrected. Unless otherwise stated, magnesium sulfate was used as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 21 instrument employing sodium chloride optics and carbon tetrachloride solutions in sodium chloride cells unless otherwise indicated and the values are reported as  $\text{cm}^{-1}$  (% absorption). The ultraviolet spectra were measured with a Cary Model 11-MS instrument with methanol solutions unless otherwise stated. The nmr spectra were obtained with a Varian Model A-60 nmr spectrometer with  $\text{CCl}_4$  solutions, unless otherwise stated, and the values are reported as  $\tau$  ( $J$ , cps) values with tetramethylsilane as an internal standard; abbreviations are sh = shoulder and b = broad band; 3 ring is three-membered ring.

(20) (a) A. L. Wilds, *ibid.*, **64**, 1421 (1942); (b) W. S. Johnson and E. S. Wesley, *ibid.*, **67**, 1745 (1945).

(12) H. O. House and R. L. Wasson, *J. Amer. Chem. Soc.*, **78**, 4394 (1950).

(13) (a) J. Volhard, *Ann.*, **296**, 14 (1897); (b) G. Soliman and R. W. West, *J. Chem. Soc.*, 53 (1944); (c) G. Kuhnmanns and J. Tübel, *J. Prakt. Chem.*, **4**, 87 (1955); (d) F. Runge and U. Koch, *Ber.*, **91**, 2171 (1958).

(14) O. Widman, *ibid.*, **49**, 2781 (1916).

(15) H. Horlander, *ibid.*, **49**, 2786 (1916).

(16) N. H. Cromwell and R. A. Setterquist, *J. Amer. Chem. Soc.*, **76**, 5752 (1954).

(17) See N. H. Cromwell and H. Hoeksema, *ibid.*, **71**, 716 (1949), for the ultraviolet spectra of a phenylhydrazone, a pyrazoline, and a pyrazole.

spectrum showed bands at 2.13–2.88 (nine aryl C–H), 5.56 (one benzyl C–H on the 3 ring), 6.93 (two methylene C–H, quartet,  $J = 18$  cps). The nmr spectrum of the higher melting isomer **2a**, mp 121–122°, which is the major product, showed bands at 2.12–2.74 (nine aryl C–H), 5.67 (one benzyl C–H on the 3 ring), 7.01 (two methylene C–H quartet,  $J = 18$ ). It is presumed that the lower melting isomer, **2b**, formed in lesser amounts, is the *cis* form while **2a** has the *trans* configuration.

**Reaction of 2a with Piperidine under Acid Catalysis.**—When a 1.0-g sample of **2a** was heated under reflux with 25-ml amounts of pure morpholine or piperidine for 3.5 hr the epoxy ketone was recovered unchanged. Acid catalysis was required to effect a reaction.

A solution of 2.0 g (0.0085 mol) of **2a** in 10 ml of piperidine was treated with 2 drops of concentrated sulfuric acid and refluxed for 24 hr. Ether was added to the cooled solution which was filtered to remove the amine salt. The ether was evaporated and the dark oil dissolved in benzene and placed on a 100-g alumina column. Elution with petroleum ether (bp 60–80°), benzene–petroleum ether, dichloromethane, 10:80 ethylacetate–dichloromethane, and finally ethyl acetate gave three main fractions: fraction 1, 0.39 g, mp 106–108°, identical with 2-benzal-1-indanone; fraction 2, 0.18-g mixture of 1 and 3; fraction 3, 0.72 g, mp 127–128°, of 2-benzyl-3-piperidino-1-indenone (**19**)<sup>7</sup> with ultraviolet maxima<sup>19</sup> at 223, 265, 318, 332, 430 m $\mu$  ( $\epsilon$  24,000, 20,600, 2500, 1700, and 3000) in *n*-hexane; infrared absorption<sup>19</sup> was at 1682 (80); nmr bands were at 2.5–3.3 (nine aryl C–H), 6.33 (singlet, two benzyl C–H), and broad bands at 6.61 (four piperidine C–H) and 8.38 (six piperidine C–H).

*Anal.* Calcd for C<sub>21</sub>H<sub>21</sub>NO: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.34; H, 6.79; N, 4.51.

A 0.13-g sample of **19** was dissolved in 5 ml of concentrated H<sub>2</sub>SO<sub>4</sub> and poured slowly into 25 ml of hot (85°) water with stirring. After standing for 12 hr the precipitated solid was removed by filtration and recrystallized from benzene–petroleum ether (bp 60–70°) to give 0.075 g (75% yield), of 2-benzyl-1,3-indandione (**20**),<sup>21</sup> mp 93–95. Infrared absorption showed bands at 1748 (68) and 1710 (85); the nmr spectrum had broad bands at 2.18–2.45, 2.82–3.0 (nine aryl C–H), and an unresolved multiplet at 6.73 (two benzyl C–H and C–H  $\alpha$  to C=O).

**2-( $\alpha$ -Chlorobenzyl)-2-hydroxy-1-indanone (3).**—A solution of 5.0 g (0.2 mol) of **2** in 50 ml of dry ether and 75 ml of dry benzene was cooled in an ice bath and saturated with dry gaseous hydrogen chloride. After standing overnight in an ice chest the reaction mixture was washed to neutrality with water and dried over anhydrous calcium sulfate, and the solvent was evaporated to yield 4.38 g (76% yield) of **3**, mp 130–131° recrystallized from benzene–petroleum ether (40–60°). Infrared absorption<sup>22</sup> (10.8 mg/ml) showed bands at 3555 (36) and 3445 (23) (OH), and at 1730 (80) and 1717 sh (76) (C=O); (5.4 mg/ml) at 3555 (24) and 3445 (8) (OH), and at 1730 (78) (C=O); (2.7 mg/ml) at 3555 (16) and 3445 (4) (OH), and at 1730 (65) (C=O). Ultraviolet maxima<sup>19</sup> were found at 250 and 295 m $\mu$  ( $\epsilon$  14,900 and 2500).

*Anal.* Calcd for C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>Cl: C, 70.40; H, 4.76; Cl, 13.50. Found: C, 70.55; H, 4.70; Cl, 13.30.

When a 0.5-g sample of **3** was heated at 90° for 1 hr with 5 ml of morpholine a near quantitative yield of **2a** resulted.

**2-Benzal-1-indanol Oxide (4).**—To a solution of 1.5 g (0.006 mol) of **2a** in 60 ml of hot methanol was added 0.7 g (0.018 mol) of NaBH<sub>4</sub> in small portions. The mixture was boiled for a few minutes and then stirred at room temperature for 1 hr. Neutralization with 2 *M* hydrochloric acid produced an oil which was extracted with ether. Evaporation of the ether and crystallization of the oil from petroleum ether, bp 60–70°, gave a 78% yield of **4**, mp 105–106°. Infrared absorption<sup>22</sup> (10 mg/ml) showed bands at 3620 (47), 3595 (46), 3445 (30) (OH); (5 mg/ml) at 3620 (37), 3595 (36), 3445 b (23) (OH); (2.5 mg/ml) at 3620 (27), 3595 (27).

*Anal.* Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>: C, 80.64; H, 5.92. Found: C, 80.56; H, 6.02.

**2-Benzyl-1,2-indandiol (5).** A.—A 2.81-g (0.01 mol) sample of **3** dissolved in 250 ml of dry benzene containing 1.0 g of sodium bicarbonate was hydrogenated over 10% Pd/C at 45 psi for 1.5 hr. The reaction mixture was filtered and cooled to produce a

solid, 1.81 g (70% yield), mp 144–145° after recrystallization from chloroform–petroleum ether, (bp 88–98°) and then from methanol and water. Infrared absorption (5 mg/ml) showed bands at 3610 (14), 3580 sh (9), 3315 b (26) (OH); (2.5 mg/ml) at 3610 (9), 3580 sh (6), 3515 b (6) (OH); (1.0 mg/ml) at 3610 (6), 3580 sh (4) (OH).

*Anal.* Calcd for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>: C, 79.34; H, 6.86. Found: C, 79.97; H, 6.71.

**B.**—A solution of 0.5 g (0.008 mol) of **4** dissolved in 25 ml of anhydrous ether was slowly added to a slurry of 1.5 g of LiAlH<sub>4</sub> (excess) in 50 ml of anhydrous ether. The mixture was stirred at room temperature for 2.5 hr and allowed to stand 12 hr. Working up the reaction mixture in the usual way gave a 60% yield of **5**.

**C.**—A solution of 2.0 g (0.008 mol) of **2a** dissolved in 150 ml of anhydrous ether was added to a slurry of 1.0 g of LiAlH<sub>4</sub> in 50 ml of anhydrous ether. The mixture was stirred for 1 hr and worked up in the usual manner to give a 64% yield of **5**.

**2-Benzyl-2-hydroxy-1-indanone (6).**—A solution of 2.0 g (0.0085 mole) of **2a** in 200 ml of anhydrous benzene containing 0.7 g of 10% Pd/C was hydrogenated at 60° for 1.5 hr at 45 psi. From this reaction mixture was obtained 1.62 g (80% yield) of **6**, mp 80–81.5° recrystallized from aqueous methanol. Ultraviolet maxima were found at 248 and 295 m $\mu$  ( $\epsilon$  15,700 and 2970). Infrared absorption (Perkin-Elmer Model 21, lithium fluoride optics) showed bands at 3554 b (32), 3447 b (10) (OH) and 1726 (87), 1717 sh (80) (C=O) (7 mg/ml); 3553 b (20), 3428 b (5) (OH) and 1723 (77) (C=O) (3 mg/ml); 3553 (7) (OH) and 1723 (70) (C=O) (1 mg/ml).

*Anal.* Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>: C, 80.64; H, 5.92. Found: C, 80.56; H, 6.02.

When the volume of benzene was reduced to 150 ml in the above hydrogenation a mixture of **5** and **6** resulted which was readily separated by recrystallization from benzene.

**2-Acetoxy-2-benzyl-1-indanone (7).**—A 0.5 g (0.002 mol) sample of **6** was dissolved in a mixture of 50 ml of acetic anhydride and 5 ml of concentrated sulfuric acid and allowed to stand at room temperature for 1 week. This reaction mixture was made basic with 6 *N* sodium hydroxide to produce a crude product which was chromatographed on Fluorisil [benzene–petroleum ether (bp 60–70°) elution] to give 0.24 g (60% yield) of **7**, mp 84–87°. Infrared absorption showed bands at 1733 (85) and 1748 (72). The nmr spectrum had bands at 2.12–2.85 (nine aryl C–H), 6.75 (singlet, two benzyl C–H), 7.17 (quartet, two methylene C–H), and 7.92 (singlet, three methyl C–H).

*Anal.* Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>: C, 77.12; H, 5.76. Found: C, 76.95; H, 5.80.

**Pyrolysis of 7.**—A solution of 1.92 g (0.007 mol) of **7** dissolved in 35 ml of benzene was dripped over a pyrolysis column packed with glass helices.<sup>23</sup> The pyrolysis was carried out under a nitrogen atmosphere at 500°. The discharge was collected in absolute ethanol. The collection solution was poured into water and the precipitate was extracted with ether. Chromatography of the crude product on alumina [benzene–petroleum ether (bp 60–70°) elution] gave 0.12 g of 2-benzal-1-indanone, mp 111–112°.

**1-Methyl-2-benzal-1-indanol Oxide (8).**—To a solution of 2.0 g (0.008 mol) of **2** in 150 ml of anhydrous ether was added 16.0 ml (0.048 mol) of commercial CH<sub>2</sub>MgBr, with stirring, under a nitrogen atmosphere. The mixture was stirred and refluxed 3 hr and poured over a 1.0 *M* NH<sub>4</sub>Cl–crushed ice mixture. The organic layer was separated and the aqueous layer was extracted twice with ether. The ether solutions were combined and washed. After drying the solution, the ether was evaporated to leave a clear oil which produced a solid on recrystallization from a CHCl<sub>3</sub>–petroleum ether (88–98°) mixture. This solid weighed 1.29 g and melted at 98–99° after chromatography on alumina and recrystallization from petroleum ether (60–70°); infrared absorption showed a band at 3620 (35) (OH).

*Anal.* Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>: C, 80.92; H, 6.39. Found: C, 80.66; H, 6.46.

**1-Phenyl-2-benzal-1-indanol Oxide (9).**—To a solution of 3.0 g (0.13 mol) of **2** in 250 ml of anhydrous ether was added with stirring under a nitrogen atmosphere a fivefold excess of freshly prepared phenyllithium. The reaction mixture was stirred and refluxed 3 hr, and then poured into a 1.0 *M* NH<sub>4</sub>Cl–crushed ice

(21) This compound was identical with an authentic sample: C. Vanags and T. Dumpis, *Dokl Akad. Nauk, SSSR*, **126**, 549 (1959).

(22) Dilution studies were carried out using a Perkin-Elmer Model 237 instrument with CCl<sub>4</sub> solution in 1.0-mm NaCl cells. Values are reported as cm<sup>-1</sup> (% absorption); sh represents a shoulder, b represents a broad band.

(23) C. S. Marvel and C. W. Hinman, *J. Amer. Chem. Soc.*, **76**, 5435 (1954).

mixture. The product was extracted with ether, washed with water, and dried. Evaporation of the ether produced a solid (5.71 g, 62% yield), mp 100–135°. Recrystallization from  $\text{CHCl}_3$ -petroleum ether (40–60°) and dilute ethanol produced the pure product, mp 143–144°; infrared absorption showed a band at 3628 (21) (OH).

*Anal.* Calcd for  $\text{C}_{22}\text{H}_{11}\text{O}_2$ : C, 84.05; H, 5.77. Found: C, 84.36; H, 5.95.

**1-Phenyl-2-benzyl-1,2-indandiol (10).**—A 0.49-g (0.0015 mol) sample of **9** in 100 ml of anhydrous benzene was hydrogenated at 45 psi for 2 hr using 0.1 g of 10% Pd/C as a catalyst. Removal of the catalyst and concentration of the solution gave 0.33 g (67% yield) of **10**, mp 138–139° recrystallized from  $\text{CHCl}_3$ -petroleum ether (bp 88–98°). Infrared absorption showed hydroxyl bands at 3605 (67) 3570 (49), 3450 (9) (20 mg/ml); 3605 (48), 3570 (30) (10 mg/ml); 3605 (31), 3570 (19) (5 mg/ml); 3605 (19), 3570 (10) (2.5 mg/ml); 3605 (11), 3570 (7) (1.2 mg/ml).

*Anal.* Calcd for  $\text{C}_{22}\text{H}_{20}\text{O}_2$ : C, 83.51; H, 6.37. Found: C, 83.58; H, 6.34.

**1-Phenyl-2-( $\alpha$ -phenylbenzyl)-1,2-indandiol (11).** A.—To a solution of 2.0 g (0.008 mol) of **2a** in 150 ml of dry ether was added a fivefold excess of  $\text{C}_6\text{H}_5\text{MgBr}$  under a nitrogen atmosphere with stirring. The mixture was stirred and refluxed for 3 hr and poured into a 1.0 M  $\text{NH}_4\text{Cl}$ -crushed ice mixture. The product was extracted into ether, washed with water, and dried. Evaporation of the ether produced a white solid, 2.06 g (62% yield), mp 208–209° after recrystallization from  $\text{CHCl}_3$ -petroleum ether (88–98°). Infrared absorption (Perkin-Elmer Model 21, lithium fluoride optics) showed hydroxyl bands at 3601 (30), 3556 (30) (7 mg/ml); 3601 (6), 3556 (6) (1 mg/ml).

*Anal.* Calcd for  $\text{C}_{25}\text{H}_{22}\text{O}_2$ : C, 85.11; H, 6.25. Found: C, 85.11; H, 6.38.

**B.**—To a solution of 0.25 g (0.0008 mol) of **9** in 50 ml of anhydrous ether was added a large excess of freshly prepared phenylmagnesium bromide. The reaction was carried out and worked up in the same manner as above; the mixture melting point of the product and an authentic sample of **11** was 208–209°.

**2-Phenyl-1,3-naphthandione (12).**—A solution of 1.89 g (0.008 mol) of **2a** in 50 ml of anhydrous ether was treated with 1.0 ml of  $\text{BF}_3$ -etherate; the mixture was stirred for 5 min, quenched with 100 ml of dry ether, and poured into 100 ml of distilled water. The crude product was isolated from the ether layer and recrystallized from chloroform to give 1.15 g (61% yield), mp 165–167°. Infrared absorption showed bands at 3602 (20), 3580 (40) (OH) and 1658 (20), 1647 (35) (C=O). Ultraviolet maxima were found at 221, 241, 289, 335, and 476  $\text{m}\mu$  ( $\epsilon$  29,000, 38,000, 5200, 1650, and 200). The nmr spectrum in  $\text{C}_6\text{D}_6\text{N}$  solvent showed bands at 0.53 (broad singlet, OH), 2.21 (1.5 methine or aromatic C-H), and 2.83–3.75 (broad band, nine aryl C-H).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{12}\text{O}_2$ : C, 81.34; H, 5.12; Found: C, 81.42; H, 5.19.

Compound **12** formed the known<sup>13a</sup> **2-phenyl-1,3-diacetoxynaphthalene (13)** on warming with acetic anhydride, mp 137–138°. Infrared absorption showed a band at 1772 (85). The nmr spectrum had bands at 1.86–2.76 (ten aryl C-H), 7.94 and 8.04 (two singlets, three methyl C-H each).

Compound **12** also formed the known<sup>13a,c,d</sup> quinhydrone (**14**)<sup>13a,c,d</sup> as a red solid on standing for 3 weeks in contact with air in a methanol solution, mp 171–173°. Ultraviolet maxima were found at 218, 240, 337, and 395  $\text{m}\mu$  ( $\epsilon$  32,000, 38,000, 3600, and 1600). Infrared absorption showed bands in chloroform at 3577 (13), 3387 (27) (OH), and 1675 (75) (C=O). The nmr spectrum in  $\text{CDCl}_3$  had bands at 1.67–2.03 (two phenolic OH, two enolic OH, and three aryl C-H adjacent to C=O), and 2.23–3.08 (15 aryl C-H).

*Anal.* Calcd for  $\text{C}_{32}\text{H}_{24}\text{O}_6$ : C, 79.00; H, 4.56. Found: C, 78.69; H, 4.63.

**5-Phenyl-3,4-indano( $\Delta^{3,4}$ -pyrazole) (15).**—To a 1.18-g (0.005 mol) sample of **2a** dissolved in 25 ml of chloroform and 5 drops of glacial acetic acid was added 0.24 ml (0.005 mol) of hydrazine

hydrate. The solution was refluxed 6 hr and diluted with ether to produce the product (0.32 g, 48% yield), mp 243–245°. Further workup of the ether solution returned 0.5 g of the epoxy ketone. Infrared absorption in chloroform showed bands at 3480 (23), 3290 (14) (NH), 1600 (13) (C=N). Ultraviolet maxima were found at 253 and 291  $\text{m}\mu$  ( $\epsilon$  17,800 and 3000).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2$ : C, 82.73; H, 5.21; N, 12.06. Found: C, 82.52; H, 5.16; N, 11.94.

**Reaction of 2a with Phenylhydrazine.**—A solution of 2.36 g (0.001 mol) of **2a** in 25 ml of ethanol was stirred while 1.43 ml (0.014 mol) of phenylhydrazine and 5 drops of glacial acetic acid were added. The solution was refluxed and stirred 2 hr, then poured over crushed ice. The suspension which formed was extracted twice with ether, and the ether extracts were combined and washed with water several times. The ether solution was dried and evaporated to give a red oil which was taken up in benzene and placed on an alumina column. Elution with benzene-petroleum ether (60–70°), dichloromethane, ethyl acetate, and 100% ethanol produced three fractions. A dark oil (0.95 g) which was the first fraction eluted, solidified to produce a product with mp 175° (after several recrystallizations from ethanol). The intermediate fraction yielded a light yellow solid, mp 88–95°, which was rechromatographed to produce a yellow solid, mp 132–134°. The final fraction produced 0.8 g of a solid, mp 153–156°.

**The Phenylhydrazone of 2-Benzal-1-indanone Oxide (16).**—The solid fraction, mp 153–156°, showed infrared absorption in chloroform at 3345 (15) (NH) and 1675 (50) (C=N) and ultraviolet maxima at 245, 295, 303, 346  $\text{m}\mu$  ( $\epsilon$  21,700, 8700, 8700, 17,100). The nmr spectrum ( $\text{CDCl}_3$ ) showed 14 aryl C-H at 2.09–3.27, one benzyl C-H (singlet) at 6.25, and two methylene C-H (quartet) at 6.63. The proton on the nitrogen is masked and probably comes at about  $\tau$  6.32.

*Anal.* Calcd for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}$ : C, 80.95; H, 5.56; N, 8.58. Found: C, 80.95; H, 5.57; N, 8.40.

**1,5-Diphenyl-4-hydroxy-3,4-indano( $\Delta^2$ -pyrazoline) (17).**—The solid fraction, mp 132–134°, showed infrared absorption in chloroform at 3595 (12), 3480 (10), 3375 (10) (OH) and 1601 (69) (C=N). Ultraviolet maxima were found at 250, 290–320, and 392  $\text{m}\mu$  ( $\epsilon$  27,000, 3000, and 22,000). The nmr absorption ( $\text{CDCl}_3$ ) showed bands for one hydroxyl proton (broad singlet) at 1.3, 14 aromatic protons at 2.42–3.08, two methylene protons (quartet) at 3.83, and one benzyl proton as a broad singlet at 7.7. This compound gave a positive Raiford test for a pyrazoline.

*Anal.* Calcd for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}$ : C, 80.95; H, 5.56; N, 8.58. Found: C, 81.10; H, 5.77; N, 8.29.

**1,5-Diphenyl-3,4-indano( $\Delta^{2,4}$ -pyrazole) (18).**—The solid fraction, mp 175°, was taken up in concentrated  $\text{H}_2\text{SO}_4$  and poured into water to precipitate the pyrazole **18**, mp 175–176°. Infrared absorption in chloroform showed a band at 1709 (69) (C=N); ultraviolet maxima were found at 265, 279, 292, and 299  $\text{m}\mu$  ( $\epsilon$  31,000, 29,000, 27,000, and 26,000). The nmr ( $\text{CDCl}_3$ ) spectrum showed 14 aryl C-H at 2.0–2.9 and two methylene C-H as a singlet at 6.2.

*Anal.* Calcd for  $\text{C}_{22}\text{H}_{16}\text{N}_2$ : C, 85.41; H, 5.54; N, 9.06. Found: C, 85.21; H, 5.28; N, 8.85.

**Registry No.**—**2a**, 16003-46-6; **2b**, 16003-47-7; **3**, 16003-48-8; **4**, 16003-49-9; **5**, 16003-50-2; **6**, 16003-51-3; **7**, 16003-52-4; **8**, 16003-53-5; **9**, 16003-54-6; **10**, 16003-55-7; **11**, 16003-56-8; **12a**, 16003-57-9; **15**, 16003-58-0; **16**, 16031-76-8; **17**, 16003-59-1; **18**, 16003-60-4; **19**, 16003-61-5.

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