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Peracid oxidation of 3-phenylindene

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PERACID OXIDATION OF
3-PHENYLINDENE

A THESIS
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BY

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AUGUST, 1969

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This project was undertaken for a two-fold purpose; first, to synthesize the desired epoxides and secondly, to study the photochemistry of these compounds. In the course of this work the epoxides could not be obtained from the phenylindenes. This paper presents the experimental results obtained, and attempts to explain the formation of the compounds obtained instead of the desired epoxides. In studying this reaction there is strong evidence to indicate that under the conditions employed epoxide formation is not occurring.
ACKNOWLEDGMENTS

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HISTORICAL

Indene oxide (indan, 1,2-epoxy; indene 2,3-oxide) is first recorded in the literature in 1919. This compound was formed in practically quantitative yield by the treatment of indene bromohydrin in ether with powdered potassium hydroxide.\(^1\) At this time Van Loon also reported the preparation of indene oxide by mechanical shaking of an anhydrous etheral solution of the bromohydrin with finely powdered potassium hydroxide. The desired product was obtained in a 92-97% yield by this method.\(^2\) Indene oxide has been prepared in a similar manner from trans-2-chloro-1-indanol by treatment "with soda," distillation of the acetone in vacuo after 15 hours, and extraction with ether.\(^3\)

---

1. The product was obtained in the form of rhombic plates\(^4\) and had the following physical constants: \(\text{mp } 31.0-31.5^\circ, \text{bp } 113 (19.5\text{mm}), d_4^{23} 1.1258, n_D^{23} 1.5627.\)

2. Van Loon reported the following physical constants for indene oxide: \(\text{mp } 31-31.5^\circ, \text{bp } 112.7-112.8^\circ (19.5\text{mm}), \text{bp } 125^\circ (31\text{mm}), \text{bp } 131^\circ (38\text{mm}), d_4^{23} 1.1258, n_D^{23} 1.5627.\)
In addition to the dehydrohalogenation of 2-halo-1-indanols, epoxyindans can be prepared by two other general methods: by reduction of 2-bromo-1-indanones; and by epoxidation of indene derivatives with a peracid. Sam and Snapp have prepared the following epoxyindans by using one or more of these three methods:

\[
\begin{array}{ccc}
\text{R}_1 & \text{R}_2 & \text{R}_3 \\
H & H & H \\
\text{CH}_3 & H & H \\
\text{C}_6\text{H}_5 & H & H \\
\text{C}_6\text{H}_5 & H & \text{CH}_3 \text{O} \\
H & \text{CH}_3 & H \\
\end{array}
\]

Thus far, no compounds which have substituents on the attached \( \text{R}_1 \) or \( \text{R}_2 \) phenyl ring of the molecule have been synthesized.

There are many ways in which the phenylindenes themselves can be prepared. Blum-Bergmann has shown that aromatically substituted pinacols could give indenes. Compound 1 has been shown to give 1,2-diphenylindene possibly by the route suggested in Figure 2.
1. 1,2-diphenylindene

\[
\begin{align*}
\text{Ar} & \quad \text{C} \quad \text{C} \quad \text{CH}_2 \quad \Phi \\
\text{OH} & \quad \text{OH} & 
\end{align*}
\]

\[\text{\(-H_2O\)}\]

\[
\begin{align*}
\text{Ar} & \quad \text{C} \quad \text{C} \quad \Phi \\
\text{OH} & 
\end{align*}
\]

2. 1,2-diphenylindene

\[
\begin{align*}
\text{Ar} & \quad \text{C} \quad \text{C} \quad \text{Ar} \\
\text{OH} & \\
\end{align*}
\]

\[\text{\(-H_2O\)}\]

\[
\text{1,2-diphenylindene}
\]
It is thought that the tertiary hydroxyl group attached to the carbon adjacent to the benzyl group is split off with a hydrogen atom from the benzyl group, and the other hydroxyl group is split off with a hydrogen atom in the ortho position of the benzyl ring. An alternate mechanism for this chemical transformation is shown in Figure 3.
The sequence in Figure 3 is preferred. By distilling compound 4 over infusorial earth in vacuo at 500-550, 3-methyl-2-phenylindene (5) was obtained; the result was confirmed by comparing 5 to a sample made by an alternate route.

\[ \text{CH}_3 \text{OH} \] \[ \overset{\text{P}_2\text{O}_5}{\text{H}} \] \[ \text{H} \] \[ \text{OH} \text{OH} \text{CH}_3 \] \[ \overset{\text{CH}_3}{\text{C} \text{C} \text{CHO}} \]

\[ \overset{\text{CH}_3}{\text{C} \text{C} \text{CH}_3} \]

\[ \overset{\text{CH}_3}{\text{C} \text{C} \text{H}_3} \]

\[ \overset{\text{CH}_3}{\text{C} \text{C} \text{OH}} \]

\[ \overset{\text{CH}_3}{\text{C} \text{C} \text{CHO}} \]

\[ \overset{\text{CH}_3}{\text{C} \text{C} \text{CH}_3} \]

\[ \overset{\text{CH}_3}{\text{C} \text{C} \text{CHO}} \]

\[ \overset{\text{CH}_3}{\text{C} \text{C} \text{CH}_3} \]

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\[ \overset{\text{CH}_3}{\text{C} \text{C} \text{CHO}} \]

\[ \overset{\text{CH}_3}{\text{C} \text{C} \text{CH}_3} \]

\[ \overset{\text{CH}_3}{\text{C} \text{C} \text{CHO}} \]
Although indenes have been obtained from aliphatic-aromatic pinacols, it is believed that this reaction is not general.

2-Phenylindene can be obtained from 3-phenylindene by subjecting the latter to red heat. J. Colonge and G. W. Weinstein showed that $\beta$-aryl ketones in carbon disulfide or petroleum ether can undergo cyclodehydration to indenes. When compound 11 was reacted with aluminum chloride in a 1:3 molar ratio, compound 12 was formed in 36% yield.

Various methylindenes have been prepared in a similar manner. Phenylindene derivatives have been prepared also by cyclization of 2,3-bis (p-hydroxyphenyl)-1,3-butadiene and its homologues using an intramolecular Friedel-Crafts reaction. Compound 13, for example, yields compound 14 by this method.
U. V. Solmsen developed a method for preparing 2-phenylindene derivatives by the reaction of an alkali metal salt of a substituted phenylacetic acid (15) with a substituted benzaldehyde (16) to form a substituted cinnamic acid (17). The product subsequently was hydrogenated to a dihydrocinnamic acid (18) and cyclized by hydrogen fluoride or phosphorous pentoxide to a substituted indanone (19). The indanone, when treated with a Grignard reagent, yielded the substituted 2-phenylindene derivative (20).
L. J. Hughes has devised a one step synthesis of 3-phenylindene by reacting benzene with a 1,3-dihalopropene or its trihalopropane precursor in the presence of a Friedel-Crafts catalyst.\textsuperscript{10,11} A molar ratio of 5:1 or 6:1 benzene/halohydrocarbon was found to be optimum with 0.14-0.40 mole of catalyst per mole of hydrocarbon; temperatures ranged from 0-50°.

P. Markov and C. Ivanov have reported a novel synthesis of benzylindene by the metatation of indene.\textsuperscript{12} Indene was added to a naphthalene-magnesium addition compound in liquid ammonia, and the magnesium salt of indene was produced. A 73% yield of benzylindene resulted when the magnesium salt was treated with benzyl chloride.

The purpose of synthesizing the indene oxide derivatives is to further the study of photochemical rearrangement mechanisms. Work has been done on the photochemistry of phenyl-oxiranes, with the work of Griffin and Kristinsson being particularly significant in this area.\textsuperscript{13}
H. Kristinsson and G. W. Griffin subjected trans-stilbene oxide (2k) in 2-methyl-2-butene to photolysis for ten hours at 40°. A 1:1 mixture of cis- (25a) and trans-2,2,3-trimethyl-1-phenylcyclopropane (25b) was obtained in 90% yield. They also isolated an oxetane (26) which was formed by addition of benzaldehyde to the solvent. The photolysis of triphenyloxirane (21b) in either 2-methyl-2-butene or a solution of 2-methyl-2-butene in benzene likewise produced the cis- and trans-2,2,3-trimethyl-phenylcyclopropane. The chief products, however, were tetraphenylethane and the oxetane product (26). Kristinsson and Griffin proposed that all these reactions involve 22 which decomposes to a carbene and a ketone, preferably by path A. These reaction steps are illustrated by Figure 27.

\[ \text{cis- and trans-2,2,3-trimethyl-1-phenylcyclopropane} \]

\[ \text{tetraphenylethane} \]

\[ \text{oxetane product (26)} \]
They also found that photolysis of tetraphenyloxirane in methanol-benzene gave practically a quantitative yield of benzhydrol methyl ether (28). The products of these reactions were separated by gas-liquid chromatography and their identification based on comparison with known samples.
Following this work, Griffin and Kristinsson studied the reaction of stilbene oxide (29) with certain olefins to gain insight into the mechanism of carbene addition.14

\[
\begin{align*}
\text{C}_6\text{H}_5 & \quad + \quad \text{C} = \text{C} \quad \xrightarrow{\text{hv}} \quad \text{R}_1\text{R}_2\text{H} \quad + \quad \text{C}_6\text{H}_5
\end{align*}
\]

The products obtained from the reaction were phenylcyclopropanes (31) and oxetanes (32). Olefins used in this study were isobutene, cis-2-butene, trans-2-butene, 2-methyl-2-butene, 2-methyl-1-butene, and 2,3-dimethyl-2-butene. The cyclopropanes were obtained in yields of 60-75%. Epimeric cyclopropanes were formed when trans-stilbene oxide was reacted with cis-2-butene, 2-methyl-2-butene, and 2-methyl-1-butene. The \textit{syn} isomer is that which has the largest number of alkyl groups \textit{cis} to the aromatic ring (or more complex groups). When \textit{trans}-stilbene oxide reacted with 2-methyl-1-butene, the \textit{syn} isomer (33) and \textit{anti} isomer (34) were formed. These isomers were separated by gas-liquid chromatography and identified by comparison of nmr data.15
Photolysis of trans-stilbene oxide with cis-2-butene and 2-methyl-1-butene, over a period of fifteen to sixty minutes, formed the least hindered (anti) isomers in greater amounts than the syn isomers. Irradiation of trans-stilbene oxide in cis-2-butene for thirty hours did not result in any change of the syn-anti ratio. No trans isomer was formed with trans-2-butene.

If epimerization of the phenyl group had occurred, the orientation of the methyl groups would have been affected. Structural changes in the epoxide may affect the course of the reaction. Triphenyl ethylene oxide, tetraphenyl ethylene oxide, methylstilbene oxide, dimethylstilbene oxide, stilbene oxide, and bisdiphenylene oxide all fragment to carbenes. Styrene oxide, however, does not fit into this pattern.

R. A. Mateer, H. Kristinsson, and G. W. Griffin studied the photochemistry of the parent compound indene oxide (35). It was found that irradiation of indene oxide in n-hexane or benzene
yielded approximately equal amounts of isochromene (37) and 2-indanone (38).

\[ \text{35} \xrightarrow{\text{hv}} \text{37} + \text{38} \]

Conversion of indene oxide to 37 probably involves cleavage of the C-C bond of the oxirane ring of 35 to give 36. The diradical on 1,4- or 1,2-hydrogen migration would yield 37. Figure 39 shows the complete sequence.

\[ \text{35} \xrightarrow{\text{hv}} \text{36} \xrightarrow{1,4\text{-H-migration}} \text{37} \]

If 1,4-hydrogen migration occurs, the product can be obtained directly. 1,2-Hydrogen migration can lead to the product by way of a bridged o-xylylene. Product 38 can be formed as indicated in Figure 41.

\[ \text{35} \xrightarrow{\text{hv}} \text{40} \xrightarrow{41} \text{38} \]
Griffin and co-workers feel that 40 is not involved in the formation of 37. This latter scheme probably involves cleavage of the $\alpha$-carbon-oxygen bond to form 40 which upon 1,2-hydrogen migration gives 38. Compound 38 can be generated thermally from compound 35. An irradiation time of three hours was found to give the best yields of isochromene. It was found that longer periods of irradiation caused the photolabile products to undergo polymerization. As the irradiation time was increased from three to twenty-four hours, however, the yield of 2-indanone increased from 32.5 to 48%. Benzene solutions (0.2 M) were used, and the relative amounts of isochromene were determined by nmr. In the course of the ultraviolet light-induced reaction of indene oxide no evidence for the expected opening of the indene oxide to a carbene was detected. The conversion of indene oxide to 2-indanone is similar to the photorearrangements that styrene oxide undergoes to give phenylacetaldehyde and that $\beta$-methylstyrene oxide undergoes to give phenylacetone.

Another interesting derivative of indene oxide whose thermal valence tautomerization and photochemistry have been studied is 2,3-diphenyldienone oxide (42).\textsuperscript{17,18} The unusual thermochromic and photochromic properties shown by this compound have been related to the equilibrium between compounds 42 and 43.
Upon the application of either strong heat or diffuse daylight, a solution of compound 42 turns red but fades on cooling or when placed in the dark. If the hot solutions are cooled, the red color persists for a longer time; if the solution is warmed again, the disappearance of the red color is accelerated. Ullman and Wilks felt the red color was due to a radical-like intermediate present in very small concentrations. When the indenone oxide was refluxed in xylene for twenty-four to forty-eight hours, the solution was no longer red and no starting material was found to be present. The intermediate species produced by thermal or ultraviolet light excitation was found to be sensitive to many reagents. The rate of fading of the red color was greatly accelerated by reaction of compound 43 with peroxides, bases, acids, mercaptans, and halogens.

Intensely colored solutions could be obtained by rapid heating to 200° or by irradiating the indenone oxide in an oxygen-free
benzene solution (320-390 mμ). Visible radiation (> 450 mμ) led to a fast and complete loss of color in the red solution. It was found that unfiltered light was not as effective in producing the colored species. The concentration of the red species present in the stationary state seems to depend on the ratio of light absorbed by the "zwitter ion" 43 as compared to the amount absorbed by the indenone oxide.

The infrared spectrum of a benzene solution of 2,3-diphenylindenone oxide previously irradiated with ultraviolet light had an intense, sharp peak at 6.38 μ and a peak of weak intensity at 8.03 μ. The former absorption is characteristic of the enolate-type group present in compound 43. A decrease in the intensity of the carbonyl peak of the 2,3-diphenylindenone oxide was also observed, indicating the loss of the carbonyl function. When this solution was bleached with visible light, the original spectrum of compound 42 was obtained. This information suggests that the 1,3-diphenyl-2-benzopyrylium-4-oxide was being converted photochemically back into the indenone oxide.

The ultraviolet spectrum of 2,3-diphenylindenone oxide in hexane (after irradiation) showed an increase in absorptivity and the appearance of new peaks at 288, 391, 408, 548, and 575 mμ. These additional peaks were lost upon irradiation with visible light. Similar results obtained when a solution of the compound was heated in mineral oil indicated the same "zwitter ion" was
being produced thermally.

Ullman and Milks assumed that 1,3-diphenyl-2-benzopyrylium-4-oxide, was the structure responsible for the red color. They attempted to trap this substance by reaction of the ring oxygen with aniline, in which case an exchange between the ring oxygen atom and the nitrogen of aniline would occur. When aniline was reacted with 2,3-diphenylindenone oxide at room temperature, the red color did not readily fade; however, on heating at 140° a reaction did occur. The product of the reaction was shown to be compound 48 by spectral data and by comparison to an authentic sample prepared by an alternate route. This reaction sequence could occur either by path C or path D in Figure 50.
According to path C, attack would have to be at the 3 position of the 2,3-substituted indanone. Since there is considerable steric hinderance to backside attack at this position, path D is the preferred path.

Additional evidence for identifying the red species as 1,3-diphenyl-2-benzopyrylium-4-oxide is given by the fact that reactive dienophiles rapidly destroy this substance. For example, if a solution of 2,3-diphenylindenone oxide is irradiated in the presence of dimethyl acetylenedicarboxylate or norbornadiene, no color is obtained. Compounds 51 and 52 can be isolated.

\[
\text{51} \quad \text{52}
\]

Since the same adducts are formed by heating 2,3-diphenylindenone oxide with the dienophiles, the likelihood of the same intermediates being produced by both methods of excitation is further increased.

Data indicates that 2,3-diphenylindenone oxide can be converted to the red-colored isomer by either a light- or heat-activated reaction. The reverse reaction occurs only photochemically. The fact that the red color fades in the dark does not in itself indicate a reversion to compound 42; decomposition could have taken place. Under atmospheric conditions decomposition is
significant and is indicated by the fact that complete disappearance of color does not occur in solutions which are carefully deoxy-
genated at room temperature. To test the reversible nature of this reaction, 2,3-diphenylindenone oxide was heated at 135° for seven hours in norbornadiene, after which no compound 42 could be detected. When a solution of compound 42 was heated in benzene at 150° for seven hours, analysis showed ten percent of 2,3-diphenylindenone oxide present. 2,3-Diphenylindenone oxide in dimethyl acetylenedicarboxylate was heated at 175° for ten minutes and gave a seventy per cent yield of adduct; the yield was not increased by prolonging the heating period. In a similar manner, 2,3-diphenylindenone oxide was heated for twenty-four minutes at 175° with diethyl succinate; eighteen per cent of the starting material was recovered. In each case, the amount of 1,3-diphenyl-2-benzo-
pyrilium-4-oxide consumed in the presence of the trapping agent exceeded the fraction used up in its absence. Apparently that amount of compound 43 which was untrapped was converted back thermally to the indenone oxide.

The 2,3-diphenylindenone oxide which was not recovered from these reactions was shown to undergo dimerization to yield a mixture consisting mainly of the two dimeric compounds, 53 and 54.
These compounds showed thermochromic activity; upon heating them, two moles of compound 43 were obtained, indicating their dimeric structure. Reaction of the two moles of compound 43 (formed by heating the dimer) with the trapping agent dimethyl acetylenedicarboxylate resulted in the formation of two moles of adduct. It has been suggested that the dimers may form by addition of the carbonyl moiety of compound 42 to the pyrylium oxide to give compound 53 or 54. Direct dimerization of compound 43 could give compound 55 or compound 56.
DISCUSSION

The objective of this study is the preparation of a series of substituted l-phenyl-1,2-epoxyindans substituted successively by H, CH₃, OCH₃, Cl, and Br in the para position. The general formula for the desired compounds is indicated in Figure 57.

![Chemical structure diagram]

The synthesis of the compound with X as a hydrogen atom already has been reported by Sam and Snapp. In the
present study, preparation of the precursor phenylindenes was accomplished through Grignard reactions, employing 1-indanone and the suitable, substituted phenylmagnesium bromide. The magnesium salt of the resulting alcohol was hydrolysed with a saturated ammonium chloride solution to form the tertiary alcohol. The alcohol was dehydrated by refluxing with phosphorous pentoxide in anhydrous benzene, and the resulting olefin was subjected to oxidation with m-chloroperbenzoic acid or perbenzoic acid. The following scheme (58) will illustrate the general synthesis used in the attempt to prepare the substituted-1-phenyl-1,2-epoxyindanes:
3-Phenylindene was prepared by the reaction of bromobenzene
and 1-indanone using the Grignard reaction. Attempted epoxidation
of this olefin with meta-chloroperbenzoic acid yielded only
1-phenyl-1-hydroxy-indan-2-one as the only isolable product.
Column chromatography showed only 3-phenylindene and the 1-phenyl-
1-hydroxy-indan-2-one to be present. Boris Weinstein attempted to
prepare 1-phenyl-1,2-epoxyindan by treating 3-phenylindene with
hydrogen peroxide and trifluoroacetic anhydride; but instead, he also obtained 1-phenyl-1-hydroxy-indan-2-one. Since the peracid oxidation failed to furnish the desired epoxide, the bromohydrin of 3-phenylindene (1-phenyl-2-bromo-indan-1-ol) was prepared and treated with alcoholic potassium hydroxide. A brown solid of undetermined composition was obtained which appeared to be polymeric in nature. The results obtained from column chromatography were inconclusive. Additional attempts to form 1-phenyl-1,2-epoxyindan by the reaction of 3-phenylindene with m-chloroperoxybenzoic acid gave only the keto alcohol.

Monoperphthalic acid was prepared, and epoxidation of the 3-phenylindene was attempted with this reagent. This reaction was run in ether and also chloroform, and in each case the 1-phenyl-1-hydroxy-indan-2-one was the product obtained.

Peroxybenzoic acid was prepared by the oxidation of benzoic acid with 70% hydrogen peroxide. A benzene solution of peroxybenzoic acid was added to a benzene solution of 3-phenylindene, and the course of the reaction was followed by thin layer and vapor phase chromatography. After a period of thirty minutes, the reaction had begun but had not proceeded to a significant extent. After one hour, the thin layer chromatogram displayed three spots in addition to the starting material. Additional samples were taken after the second and
third hours of reaction. Three spots in addition to starting material were distinctly detected by thin layer chromatography, and according to the vapor-phase chromatogram, the amount of starting material was decreasing. Although vapor-phase chromatography showed that starting material was being consumed, attempts to follow the formation of products were inconclusive because of decomposition occurring on the column. The infrared spectrum of the reaction mixture showed peaks at 2.8 λ and 5.8 λ, absorptions which are characteristic of the hydroxyl and carbonyl functional groups. These absorptions could be detected after one half hour of reaction time, and the intensity of these two peaks increased with time of reaction. After one half hour an nmr spectrum of the reaction mixture revealed new peaks at 2.0 γ, a series of peaks at 4.2 γ, a series of peaks at 6.6-6.8 γ, and a peak at 7.0 γ. Over the three-hour time interval, the triplet at 3.4 γ assigned to the methine proton of 3-phenylindene and the doublet at 6.5 γ assigned to the methylene protons of 3-phenylindene both decreased in intensity. The decrease in these peak intensities indicated that starting material was being consumed. The appearance of the new peaks indicated the formation of a product or products. The intensity of the new peaks increased as the time of reaction increased. In order to test for the presence of an epoxide, ammonia was bubbled through a small portion of this reaction mixture. However, thin layer and gas chromatographic analysis indicated no apparent reaction; this information strongly indicates that there is an apparent
absence of epoxide. A white solid was isolated from the reaction mixture by crystallization, and on the basis of infrared and nmr spectra and an elemental analysis it was assigned the structure of 1-phenyl-l-hydroxy-2-indanylbenzoate. The residual oil was chromatographed on a Florisil column, but the results were inconclusive.

A chloroform solution of 3-phenylindene was treated with a benzene solution of the peroxybenzoic acid at a lower temperature and for a longer reaction period, and the product obtained was 1-phenyl-l,2-dihydroxy-indan.

3-Phenylindene was treated with peroxybenzoic acid in chloroform according to the time and temperature specified by Snapp. The product isolated from the reaction mixture was 1-phenyl-l-hydroxy-2-indanyl-benzoate.

3,4-Dihydro-l-phenylnaphthalene was prepared by a multi-stage synthesis beginning with the reaction of benzene with \( \gamma \)-butyrolactone in the presence of aluminum chloride to furnish \( \alpha \)-tetralone.\(^{26}\) The \( \alpha \)-tetralone was reacted with phenylmagnesium bromide, and after dehydration of the resulting alcohol with phosphorous pentoxide, 3,4-dihydro-l-phenylnaphthalene was obtained. The epoxidation of 3,4-dihydro-l-phenylnaphthalene was carried out in an ethereal solution of peroxybenzoic acid. This reaction was attempted because this olefin is very similar in structure to 3-phenylindene, with the exception of an additional
methylene group. It was thought that this reaction might provide some helpful clues relative to the preparation of the epoxyindans. A white solid was obtained from this reaction; the infrared spectrum showed the hydroxyl and carbonyl functional groups to be absent, and the presence of a peak at 11.2 μ is typical of epoxides. The nmr spectrum of this material shows this substance to be the desired product 1-phenyl-1,2-epoxy-3,4-dihyronaphthalene. Repeated recrystallizations failed to furnish the compound with a sharp melting point. The white solid was subjected to column chromatography on a Florisil column. Two yellow bands were eluted from the column with distinctly different infrared and nmr spectra and each was different with respect to the white solid. The initial yellow band furnished a compound containing the hydroxyl and carbonyl moieties; this compound is assigned the structure 1-phenyl-1-hydroxy-2-keto-3,4-dihyronaphthalene. The second band provided a compound containing the hydroxyl group but no carbonyl group. This substance is the glycol 1-phenyl-1,2-dihydroxy-3,4-dihyronaphthalene. Chemical reaction occurred on the column.

3-p-Tolylindene was prepared by the reaction of p-bromotoluene and 1-indanone through the Grignard reaction. This olefin was subjected to oxidation by perbenzoic acid in chloroform and also ether. The infrared spectrum of both reaction mixtures were identical. Repeated attempts at recrystallization failed, so the latter reaction mixture was analyzed by column chromatography. An orange oil was obtained, and the infrared and nmr spectra of
this material showed this substance to be the hydroxy-ketone 1-p-tolyl-1-hydroxy-indan-2-one. An attempt to purify this compound by reaction with Girard's Reagent T was unsuccessful; this compound also failed to form a 2,4-dinitrophenylhydrazone.

The difficulties encountered in attempting to prepare the epoxyindans is understandable. For example, treatment of indene with perbenzoic acid gives poor results as far as the formation of indene oxide is concerned. The attempted epoxidation of 2-phenylindene with perbenzoic acid was unsuccessful, and only the 2-phenylindene could be recovered from the reaction mixture.

Windhaus has studied the various reactions of perbenzoic acid with unsaturated compounds. He has shown that when ergosterol (59) was reacted with one mole of perbenzoic acid, compound 60 was formed. It is thought that this reaction does produce the epoxide, but since the epoxide is allylic, it is readily cleaved to the hydroxy-benzoate (60).
The exocyclic double bond is very unreactive.

When lumisterol (61) is reacted with peroxybenzoic acid for a short time, the epoxide (62) is formed. The epoxide can be hydrolyzed by brief heating in water to give compound 63.

If lumisterol is treated with a chloroform solution of perbenzoic acid, or if the benzene solution of perbenzoic acid and lumisterol is left standing for three days, compound 64 is produced.

Compound 64 can be saponified to compound 65; compound 65 on further oxidation can be converted to compound 66. Figure 67 illustrates the entire sequence.
The cleavage of compound 62 is due to the acidity of the reagent and the allylic nature of the compound. The allylic double bond favors development of carbonium ion character which makes this site attractive for the nucleophile to attack. Figure 71 illustrates the cleavage of compound 62.
Since the 3-phenylindenes have a phenyl group attached directly to the carbon containing the olefinic linkage, these compounds are closely related to these steroids with regard to peracid oxidation. The phenyl group also can favor the development of a carbonium ion just as the allylic double bond. In fact, Weinstein has postulated a similar mechanism for the formation of 1-phenyl-1-hydroxy-indan-2-one from the oxidation of 3-phenylindene.33
EXPERIMENTAL

3-Phenylindene

Into a three-neck 500-ml flask was placed 5.7 g (0.24 mol) of magnesium in 100 ml of dry ether with a few mg of iodine. Several ml of dry bromobenzene were added, and the flask was placed in a hot water bath for 2 or 3 min. During this time the iodine color disappeared, and the solution became cloudy; bubbling indicated that the reaction had started. A solution of 37.85 g (0.24 mol) of bromobenzene in 100 ml of dry ether was added over a period of approximately 1 hr; during this time the solution turned dark brown. The reaction mixture was heated on a steam bath for 30 min until it was evident that the reaction was complete. A solution of 25 g (0.19 mol) of 1-indanone in 50 ml of dry ether was then added over a period of 1 hr and 15 min; the resulting mixture was stirred for 3 hr and 30 min. The solution was treated with 35 ml of a saturated ammonium chloride solution. The ether layer was filtered, dried (MgSO₄), and evaporated to yield 37.60 g (0.18 mol) of a brownish-yellow oil, 1-phenyl-1-indanol. This crude 1-phenyl-1-
indanol was refluxed in 170 ml of dry thiophene-free benzene with 25.55 (0.18 mol) of phosphorous pentoxide for 25 min. The benzene layer was cooled, decanted, and washed with four 25 ml portions of 3% sodium hydroxide followed by 50 ml of water. The benzene layer was dried (MgSO₄), the benzene evaporated, and the orange oil was distilled at reduced pressure to yield 23.83 g (0.12 mol) of 3-phenylindene, bp 132-133 (0.25 mm). The product was produced in 63% yield.

1-Phenyl-1-Hydroxy-Indan-2-one

A solution of 10.3 g (0.06 mol) of meta-chloroperbenzoic acid in 200 ml of dry, acid-free, chloroform was added over a period of 2 hr and 30 min to a stirred solution of 9.6 g (0.05 mol) of 3-phenylindene in 50 ml of dry, acid-free, chloroform. The reaction mixture was maintained at 0° during the addition of the m-chloroperbenzoic acid and was stirred an additional 7 hours in the ice bath and for 12 hr at room temperature. The pink mixture was filtered, and the chloroform layer was extracted with three 100-ml portions of cold 10% sodium hydroxide, followed by two 100-ml portions of water, and then dried (Na₂SO₄). The chloroform was evaporated to dryness to yield a red oil which upon recrystallization from benzene-cyclohexane yielded 3.44 g (0.015 mol) of 1-phenyl-1-hydroxy-indan-2-one, mp 125-126°. This product was obtained in 30% yield.

**1-Phenyl-2-Bromo-Indan-1-ol**

A mixture of 23.83 g (0.124 mol) of 3-phenylindene, 3.47 g of Tide, and 750 ml of water was heated to 80°, and stirred vigorously to promote good emulsion formation. To this mixture was added a solution of 19.84 g (0.13 mol) of bromine and 49.6 g (0.48 mol) of sodium bromide in 750 ml of water over a period of 2-2.5 hr with vigorous stirring. The temperature was maintained at 80°, and the emulsion was stirred for 4 hr. The aqueous layer was decanted, and the red oil was stirred an additional 4 hr with 1000 ml of fresh, cold water. The aqueous layer was again decanted, and the red oil was dried to give 14.11 g of the crude bromohydrin. The red oil was triturated with petroleum ether to give 9.74 g (0.03 mol) of a light-brown to white solid, mp 128-132°. This bromohydrin was obtained in a 24% yield.

**Attempted Epoxidation of 1-Phenyl-2-Bromo-Indan-1-ol**

A mixture of 14.94 g (0.05 mol) of 1-phenyl-2-bromo-indan-1-ol, 45.45 g (0.81 mol) of potassium hydroxide, and 650 ml of methanol was stirred vigorously for 4 hr in a hot water bath. The mixture was filtered, and a brown solid was obtained. Attempts to obtain a vapor phase chromatogram and a nuclear magnetic resonance spectrum of this material were unsuccessful, indicating that the substance was a polymer. The methanol was evaporated, and nothing of consequence was left.
Monoperphthalic Acid

A 1-l. three-neck flask was equipped with a mechanical stirrer, thermometer, and dropping funnel. A solution of 62 g (0.5 mol) of sodium carbonate monohydrate in 250 ml of water was placed in the flask and cooled to 0° in an ice-salt bath. To this solution was added 69 g (63 ml, 0.6 mol) of 30% hydrogen peroxide in a single portion. While the temperature was kept at -5 to 0°, 74 g (0.5 mol) of phthalic anhydride, previously ground to a powder with mortar and pestle, was added.

The reaction mixture was stirred vigorously for 30 min while the temperature was maintained at -5 to 0°. The resulting suspension was poured into a 2-l. separatory funnel, shaken with 350 ml of ether, and slowly acidified with an ice-cold solution of 30 ml of sulfuric acid in 150 ml of water. The suspension was extracted with two additional 150-ml portions of ether. The combined ether layers were washed with two 200-ml portions of 40% ammonium sulfate solution, and the ether layers were dried (over 50 g of anhydrous MgSO₄) overnight in a refrigerator. The ether was evaporated on a rotary evaporator to give 73.82 g of a white solid.

A 0.2 g sample of the white solid was dissolved in a small volume of ether and 30 ml of 20% potassium iodide solution was added. After 10 min the liberated iodine was titrated with standardized 0.1 N sodium thiosulfate. The peracid content was determined to be 57-58%. 
1-Phenyl-1-Hydroxy-Indan-2-one

A solution of 22.4 g (0.07 mole of 57% peracid) of monoperphthalic acid in 200 ml of anhydrous ether was added over a period of 1 hr and 30 min to a stirred solution of 9.6 g (0.05 mol) of 3-phenylindene in 50 ml of anhydrous ether. The reaction mixture was maintained at -5 to 0° during the addition of the monoperphthalic acid and was stirred an additional 2 hr and 30 min at this temperature. The mixture was stirred at room temperature for 6 hr. The mixture was filtered, and the ether layer was extracted with three 100-ml portions of ice-cold 10% sodium hydroxide, followed by two 100-ml portions of water, and then dried (Na₂SO₄). The ether was evaporated, and a crystalline solid appeared in the yellow oil upon cooling. The oil was triturated with cyclohexane to yield 1.1 g (0.005 mol) of 1-phenyl-1-hydroxy-indan-2-one, mp 125-128°. The infrared and nmr spectra were identical to the previous sample of this material synthesized.

Peroxybenzoic Acid

To a slurry of 36.6 g (0.3 mol) of benzoic acid in 86.5 g (0.9 mol) of methanesulfonic acid was added 22.0 g (0.45 mol) of 70% hydrogen peroxide. The reaction mixture was stirred by means of a magnetic stirrer, and the reaction temperature was maintained at 25-30 by means of an ice-water bath. The hydrogen peroxide was added over a period of approximately 30 min.
The solution was stirred for 2 hr and then cooled to 15°C. To the reaction mixture, 50.0 g of ice and 75 ml of ice-cold saturated ammonium sulfate solution were added in sequence. During this addition, the temperature of the solution was kept at 20-25°C by means of an ice-water bath. The reaction mixture was transferred to a 500-ml separatory funnel and extracted with three 50-ml portions of benzene. The combined benzene extracts were washed with two 15-ml portions of ice-cold saturated ammonium sulfate solution, dried (Na₂SO₄), and placed in a refrigerator. Iodometric titration of an aliquot of the benzene solution showed that 1 ml of the benzene solution contained 0.1200 g of peroxybenzoic acid. This yield represents a 57-58% conversion to the peracid.

Peroxybenzoic acid was prepared a second time with less cooling of the initial reaction mixture. In this instance the benzoic acid completely dissolved, and the peracid yield was 75.8%. Subsequent preparations of this compound resulted in 85-90% conversion to the peracid.

1-Phenyl-1-Hydroxy-2-Indanyl-Benzote

To 4.8 g (0.025 mol) of 3-phenylindene in 50 ml of benzene was added 41 ml of a benzene solution of 4.92 g (0.035 mol of the 58% peracid) of peroxybenzoic acid. The solution was stirred, and the reaction temperature was maintained at -5 to 0°C by means of an acetone-ice bath. After reaction times of 0.5, 1, 2, and 3 hr, samples were taken from the reaction mixture for analysis.
After stirring the reaction mixture for 3 hr, the solution was extracted with dilute base, washed with water, and dried (Na$_2$SO$_4$). The benzene was removed on a rotary evaporator, and the residue was recrystallized from carbon tetrachloride-petroleum ether to give 1.5 g (0.005 mol) of 1-phenyl-1-hydroxy-2-indanyl-benzoate, mp 128-129.

**Anal.** Calcd. for C$_{22}$H$_{18}$O$_3$: C, 80.00; H, 5.46. Found: C, 79.46; H, 5.54.

1-Phenyl-1,2-Dihydroxy-Indan

To 4.8 g (0.025 mol) of 3-phenylindene in 100 ml of chloroform was added 41 ml of a benzene solution of 4.92 g (0.035 mol of the 58% peracid) of peroxybenzoic acid. The solution was stirred for 8 hr, and the temperature was maintained at -15 to -10 by means of an acetone-dry ice bath. The solution was allowed to come to room temperature over the next 12 hr. The solution was washed with dilute base, washed with water, and dried (Na$_2$SO$_4$). The solvents were removed with a rotary evaporator at room temperature, and the resulting oil was recrystallized from ethanol to afford 1.2 g (0.005 mol) of 1-phenyl-1,2-dihydroxy-indan, mp 99-100.

**Anal.** Calcd. for C$_{15}$H$_{14}$O$_2$: C, 79.65; H, 6.20. Found: C, 79.49; H, 6.24.
1-Phenyl-1-Hydroxy-2-Indanyl-Benzoate

The procedure followed here is that of Snapp.\textsuperscript{35}

A solution of 4.4 g (0.024 mol of 75.8\% peracid) of peroxynbenzoic acid in 75 ml of dry, acid-free chloroform was added over a period of 1 hr to a stirred solution of 3.35 g (0.017 mol) of 3-phenylindenc in 25 ml of dry, acid-free chloroform. The reaction mixture was maintained at 0 during the addition. The solution was stirred for 4 hr in an acetone-ice bath at 0-5\textdegree and for 6 hr at room temperature. The solution was extracted with three 50-ml portions of ice-cold 10\% sodium hydroxide solution, followed by two 50-ml portions of water, and dried (Na\textsubscript{2}SO\textsubscript{4}). The chloroform was removed on a rotary evaporator at room temperature, leaving a white solid in the flask. Recrystallization of the solid from ethanol gave 1.2 g (0.004 mol) of 1-phenyl-1-hydroxy-2-indanyl-benzoate, mp 127-128\textdegree. The infrared and nmr spectra were identical with the sample of this compound previously prepared.

\textsuperscript{\small A - Tetralone}

A 5-l three-neck flask was equipped with an electric stirrer and condenser with a drying tube of calcium chloride. One liter of anhydrous, thiophene-free benzene and 104 g (1.21 mol) of \textit{\textgamma}-butyrolactone were placed in the flask. Six hundred grams (4.5 mol) of anhydrous aluminum chloride were placed in an Erlenmeyer flask and slowly added to the reaction mixture over a period of approximatel
5 hr. During the course of the reaction the mixture became dark brown, refluxed gently, and hydrogen chloride was evolved. The mixture was heated over night on a heating mantel. The mixture was cooled to room temperature and poured slowly into a beaker containing 3 kg of crushed ice and 500 ml of concentrated hydrochloric acid. The lower aqueous layer was separated and extracted with 500 ml of toluene. The brown, organic upper layer and toluene extracts were combined and washed successively with water, 20% potassium hydroxide solution, water, and distilled at reduced pressure to remove benzene, toluene, and traces of water. The residue was distilled at reduced pressure to give 141 g (0.9 mol) of \( \alpha \)-tetralone, bp 78-82 (0.3 mm). The ketone was obtained in 74% yield.

3,4-Dihydro-1-Phenyl-Naphthalene (1-Phenyldialin)

A solution of phenylmagnesium bromide was prepared from 11 g (0.45 mol) of magnesium, 75 g (0.48 mol) of bromobenzene, and 175 ml of anhydrous ether. A solution of 58.4 g (0.4 mol) of \( \alpha \)-tetralone in 60 ml of dry ether was added over a period of 30 min. The mixture was heated on a steam bath for 30 min and allowed to stand for 1 hr. The mixture was then poured into a beaker containing 250 g of ice and 40 ml of concentrated hydrochloric acid. The ether layer was separated and steam distilled until 4.5 l of distillate were collected. The reddish-orange oil was separated from the aqueous layer, and 80 ml of ether was added. The
mixture was dried (MgSO₄) over night. The ether was removed on a rotary evaporator to yield 53.9 g (0.24 mol) of the crude alcohol. The crude alcohol was heated for 25 min with 34.1 g (0.24 mol) of phosphorous pentoxide in 170 ml of anhydrous benzene. The benzene layer was washed successively with dilute base, water, and dried (MgSO₄). The benzene was removed on a rotary evaporator, and the residue was distilled at reduced pressure to furnish 23.72 g (0.11 mol) of 1-phenyldialin, bp 125-130 ° (0.5 mm). This olefin was obtained in a yield of 27.5%.

1-Phenyl-1,2-Epoxy-3,4-Dihydro-Naphthalene

A solution of 6.9 g (0.038 mole of 75.8% peracid) of perbenzoic acid in 65 ml of anhydrous ether was added to a stirred solution of 5.63 g (0.027 mole) of 3,4-dihydro-1-phenyl-naphthalene in 50 ml of anhydrous ether. The temperature of the reaction was maintained at -5-0 ° during the addition period of 1 hr. The reaction mixture was stirred an additional 8 hr in the acetone-ice bath at 0. The reaction mixture was then washed successively with three 50-ml portions of ice-cold 10% sodium hydroxide solution followed by two 50-ml portions of water and dried (Na₂SO₄). When the ether was removed on a rotary evaporator, a white solid was left in the flask. This epoxide was obtained in a yield of 60% (3.6 g, 0.016 mol). Recrystallizations from benzene-petroleum ether and also ethanol failed to produce the compound with a sharp melting point. When the white solid was analyzed by column
chromatography, a reaction occurred on the column and the epoxide was not isolated; instead, a keto-alcohol and a glycol were isolated.

3-\(p\)-Tolylindene

Into a 3-neck 1 l round-bottom flask equipped with magnetic stirrer, dropping funnel, condenser, and thermometer was placed 11.4 g (0.47 mol) of magnesium in 300 ml of anhydrous ether; a few mg of iodine were added. A few ml of a solution of 82.10 g (0.48 mol) of \(p\)-bromotoluene in 100 ml of dry ether were added. The flask was immersed in a hot water bath for several minutes until the iodine color disappeared and vigorous bubbling ensued. The remainder of the \(p\)-bromotoluene solution was added over a period of 1 hr and 20 min. The resulting reaction mixture was heated on a hot water bath for 0.5 hr; most of the magnesium had dissolved by this time. Next, a solution of 50.0 g (0.38 mol) of 1-indanone in 100 ml of anhydrous ether was added dropwise over a period of approximately 1 hr. The dark brown solution was stirred for 4 hr and then slowly hydrolyzed over a period of 1 hr by the addition of 70 ml of a saturated ammonium chloride solution. The ether layer was filtered, dried (\(\text{MgSO}_4\)), and the ether evaporated to yield 71.7 g (0.32 mol) of a yellow oil, 1-\(p\)-tolyl-1-indanol. The crude alcohol was refluxed with 45.42 g (0.32 mol) of phosphorous pentoxide in 300 ml of anhydrous benzene for 25 min. The benzene layer was cooled, decanted, and divided into two equal portions. Each portion was washed with three 50-ml
portions of ice-cold 5% sodium hydroxide, followed by two 50-ml portions of water. The combined benzene layers were dried (MgSO₄), the benzene removed on a rotary evaporator, and the orange oil vacuum-distilled to furnish 41.16 g (0.20 mol) of 3-p-tolylindene, bp 136-138° (0.35 mm). This amount represents a 62.5% yield of the olefin.

1-p-Tolyl-1-hydroxy-indan-2-one

A solution of 11.0 g (0.07 mol) of 88% peracid of peroxycbenzoic acid in 150 ml of anhydrous ether was added over a period of 1 hr to a stirred solution of 10.3 g (0.05 mol) of 3-p-tolylindene in 50 ml of anhydrous ether. The reaction mixture was maintained at 0° during the addition of the perbenzoic acid solution and was stirred an additional 4 hr at this temperature and 6 hr at room temperature. The reaction mixture was extracted with dilute base, washed with water, and dried (Na₂SO₄). The ether was removed by means of a rotary evaporator to yield a light yellow oil. Repeated attempts at recrystallization were unsuccessful so the oil was chromatographed to yield an orange oil, 1-p-tolyl-1-hydroxy-indan-2-one. Infrared and nmr spectra confirm this structure. The compound could not be obtained in pure form; it failed to react with both 2,4-dinitrophenylhydrazine and Girard's Reagent T. When chloroform was employed as the solvent, an identical reaction mixture was obtained.
SUMMARY

The oxidation of 3-phenylindene afforded three different compounds: 1-phenyl-1-hydroxy-indan-2-one, 1-phenyl-1,2-dihydroxyindan, and 1-phenyl-1-hydroxy-2-indanyl-benzoate. All reactions failed to produce the desired compound 1-phenyl-1,2-epoxyindan. The oxidation of 3-p-tolyldene produced 1-p-tolyl-1-hydroxy-indan-2-one; again, the desired epoxide was not isolated. In the case of the naphthalene derivative, 1-phenylindalin, an epoxide was obtained in high yield by peracid oxidation.

These results indicate that the phenylindene oxides, if present at all, are so reactive under the conditions employed that their isolation is not feasible. It is also quite possible that epoxide formation may fail to occur, particularly in the reaction producing the hydroxy-benzoate. It appears that the six-member ring of the naphthalene derivative gives this epoxide an increased stability not present in the five-member ring of the phenylindene nucleus.
BIBLIOGRAPHY

5. O. Blum-Bergman, *Ber.*, 65 (B), 109, (1932).
   (1964).
17. E. F. Ullman and J. E. Milks, *J. Amer. Chem. Soc.*, 84, 1315, 
   (1962).
   93, (1963).
25. T. C. Snapp, Jr., Dissertation, University of Mississippi, 
   University, Mississippi, (1965).
   (1936).

29. T. C. Snapp, Jr., personal communication


32. Ibid.


34. The 70% hydrogen peroxide used in this preparation was furnished by FMC Corporation Inorganic Chemicals Division Buffalo, New York.

35. T. C. Snapp, Jr., Dissertation, University of Mississippi, University, Mississippi, (1965).
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