LIQUID-PHASE OXIDATION OF *p*-CYMENE: NATURE OF INTER-MEDIATE HYDROPEROXIDES AND RELATIVE ACTIVITY OF THE ALKYL GROUPS¹

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ABSTRACT

A study has been made of the liquid-phase oxidation of p-cymene with elemental oxygen using emulsion and photochemical procedures with the object of determining (a) the nature of the resulting hydroperoxides and their decomposition products, and (b) the relative activity of the methyl and isopropyl side chains.

The following compounds have been shown to be present in the emulsion oxidation product: 2-p-tolyl-2-propyl hydroperoxide, 2-p-tolyl-2-propanol, pisopropylbenzyl alcohol, p-methylacetophenone, cumic acid, $p \cdot (\alpha \cdot hydro$ peroxyisopropyl) benzoic acid, $p \cdot (\alpha \cdot hydroxyisopropyl)$ benzoic acid, and $p \cdot acetyl$ benzoic acid. The two hydroperoxides have been isolated and characterized.By chromatographic separation of the carboxylic acids and fractional distillationof the alcohols formed by lithium aluminum hydride reduction of all otherproducts, the relative susceptibility of the methyl and isopropyl groups tooxidative attack has been shown to be 1:4.

In the photochemical oxidation, hydroperoxide decomposition was very small and the product was shown to consist of 20% p-isopropylbenzyl hydroperoxide and 80% of 2-*p*-tolyl-2-propyl hydroperoxide. The relative extent of oxidative attack at the two positions was therefore identical in the two oxidations.

The preferred position of attack by elemental oxygen in the liquid-phase oxidation of alkyl benzenes has been shown to be the side-chain carbon directly attached to the aromatic ring, provided that this carbon is not quaternary (17). The initial products of such oxidations are hydroperoxides and, under appropriate conditions, these may be isolated and characterized. Included among the known hydroperoxides of this type are p-xylyl hydroperoxide (8), 1-phenylethyl hydroperoxide (8), and 2-phenyl-2-propyl hydroperoxide (9, 1). The hydrocarbon p-cymene, I, provides two centers for attack, the methyl carbon and the tertiary carbon of the isopropyl group, and two isomeric hydroperoxides, 2-p-tolyl-2-propyl hydroperoxide, II, and p-isopropylbenzyl hydroperoxide, III, may, therefore, be formed.



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Helberger, Rebay, and Fettback (6) studied the oxidation of p-cymene with oxygen in the presence of sunlight and isolated the sodium salt of the hydroperoxide by precipitation with aqueous sodium hydroxide. The hydroperoxide was considered to have structure III since cuminaldehyde could be isolated from the products of the decomposition of the salt in boiling water. Lorand (12), on the other hand, has reported that the sodium sulphide reduction of the hydroperoxide formed by oxidation of p-cymene with oxygen in the presence of aqueous alkali furnished a product consisting of 90% 2-p-tolyl-2-propanol and 10% p-methylacetophenone. The apparent absence of p-isopropylbenzyl alcohol in the reduction product would suggest that the tertiary hydroperoxide, II, was the only hydroperoxide formed by oxidation under these conditions.

The seemingly contradictory results obtained using the two oxidation methods are indeed surprising since current ideas concerning the mechanism of hydrocarbon oxidation (2) would strongly suggest that a product of similar composition should be obtained in each case. The present paper reports the results of a reinvestigation of the oxidation of p-cymene in which an effort has been made to determine quantitatively the composition of the total oxidation product formed using the two oxidation procedures. In addition to establishing the nature of the hydroperoxide product, this study has provided an accurate measure of the relative activity of the methyl and isopropyl groups toward oxidative attack.

Emulsion Oxidation

The oxidation in the presence of aqueous alkali was carried out using a procedure recently developed by Armstrong, Hall, and Quinn (1) for the preparation of tertiary hydroperoxides. Oxygen was passed into an emulsion of p-cymene and aqueous sodium carbonate in the presence of sodium stearate as the emulsifying agent and a small amount of cymyl hydroperoxide as the initiator. Oxidations were studied at 85 and 60°C. At the higher temperature the reaction was continued until the emulsion had broken, at which point the hydroperoxide concentration of the hydrocarbon had reached 40% by weight. At 60°C., however, the oxidation was very slow and the reaction was interrupted when a 19% hydroperoxide concentration had been attained.

On completion of an oxidation, the aqueous layer of the reaction product was separated and acidified, and the precipitated acids were then analyzed by a column partition chromatographic method. Four compounds were obtained: cumic acid, p-acetylbenzoic acid, p-(α -hydroxyisopropyl)benzoic acid, and a new hydroperoxide, p-(α -hydroperoxyisopropyl)benzoic acid. The structure of the latter was established by (a) neutralization equivalent, (b) peroxidic oxygen analysis, (c) reduction to the p-(α -hydroxyisopropyl)benzoic acid, and (d) metal-catalyzed decomposition to the hydroxy acid and p-acetylbenzoic acid.

The organic layer was divided into two portions. Aliquot I was reduced with lithium aluminum hydride to furnish a product which was separated into two fractions by fractional distillation. The lower-boiling fraction was a mixture of the tertiary and secondary alcohols, 2-p-tolyl-2-propanol and 1-p-tolylethanol, respectively, with the former predominating. The greater part of the tertiary alcohol resulted from the reduction of the tertiary hydroperoxide, II, although some was formed by decomposition of this hydroperoxide during the oxidation. The secondary alcohol was formed by reduction of p-methylacetophenone, a second decomposition product of the tertiary hydroperoxide. The smaller second fraction was the primary alcohol, p-isopropylbenzyl alcohol, formed from the primary hydroperoxide, III, by decomposition during the oxidation and by reduction with lithium aluminum hydride. The results of this fractionation, combined with those of the chromatographic analysis of the acids and the ketone analysis on Aliquot II, permitted the calculation of the relative extent of oxidative attack at the two available positions.

In order to obtain additional information on the composition of the oxidation product as well as to determine the nature of the hydroperoxide isolated by the sodium salt precipitation, the second portion of the organic layer, *Aliquot* II, was treated with a concentrated solution of sodium hydroxide. The insoluble hydroperoxide salt was filtered, the hydroperoxide liberated with carbon dioxide and reduced with lithium aluminum hydride to yield 2-p-tolyl-2-propanol in high yield. The absence of p-isopropylbenzyl alcohol in the reduction product established that the hydroperoxide actually *isolated* as the sodium salt from the products of the emulsion oxidation was the tertiary compound, II, uncontaminated with the primary isomer, III. The small organic layer of the filtrate from the sodium salt filtration was analyzed for its ketone (p-methylacetophenone) content and was then fractionated. A single fraction consisting of the tertiary alcohol, 2-p-tolyl-2-propanol plus a small amount of p-methylacetophenone was obtained.

The composition of the product from emulsion oxidations at 85 and 60°C., expressed as mole %, is shown in Table I.

| | Mole % | |
|--|--|--|
| Product | 85°C. Run | 60°C. Run |
| 2-p-Tolyl-2-propyl hydroperoxide 2-p-Tolyl-2-propanol p-Isopropylbenzyl hydroperoxide plus p-isopropylbenzyl alcohol p-Methylacetophenone Cumic acid $p-(\alpha-Hydroperoxyisopropyl)$ benzoic acid $p-(\alpha-Hydroxyisopropyl)$ benzoic acid p-Acetylbenzoic acid | $\begin{array}{r} 49.4\\ 22.3\\ 7.5\\ 3.4\\ 11.7\\ 2.9\\ 1.7\\ 1.1\end{array}$ | $\begin{array}{r} 59.2 \\ 12.1 \\ 10.3 \\ 7.0 \\ 9.6 \\ 1.2 \\ 0.4 \\ 0.2 \end{array}$ |

 TABLE I

 Composition of the products of the emulsion oxidation

Photochemical Oxidation

The procedure used in the so-called photochemical oxidation of p-cymene was similar to that described by Helberger *et al.* except that a mercury-vapor lamp was used as a source of illumination rather than sunlight. The reaction,

which was carried out at 60°C. only, was much slower than the emulsion oxidation and therefore was stopped when the hydroperoxide concentration was 5.5%.

Preliminary work had shown that carboxylic acids were present in the oxidation product to only a very small extent (less than 0.6% of the oxidized hydrocarbon) and consisted mainly of cumic acid. For this reason, the total reaction mixture was reduced directly with lithium aluminum hydride without making a preliminary alkaline extraction. Fractionation of the reduction product furnished the tertiary and primary alcohols, 2-p-tolyl-2-propanol and p-isopropylbenzyl alcohol, respectively. The total weight of the reduction product was almost identical with the weight expected from the reduction of the known amount of hydroperoxide in the oxidation mixture. Since such reductions are practically quantitative it was concluded that the photochemical oxidation product was almost entirely in the form of hydroperoxides. The composition of the product calculated on the basis that the total tertiary alcohol was formed by reduction of the primary hydroperoxide, III, was 79.5% II and 20.5% III.

Relative Activity of the Methyl and Isopropyl Groups

The extent of oxidative attack at the primary and tertiary α -carbon atoms *p*-cymene in the emulsion and photochemical oxidation is shown in Table II.

| Per cent attack a | T PRIMARY AN | D TERTIARY a- | CARBON ATOMS | |
|-----------------------------------|---|---------------|---------------|--|
| Position of attack | Emulsion oxidation | | Photochemical | |
| | 85°C. | 60°C. | 60°C. | |
| Primary carbon Tertiary carbon | $\begin{array}{c} 22.0 \\ 78.0 \end{array}$ | 20.8 79.2 | 20.5 79.5 | |

TABLE II PER CENT ATTACK AT PRIMARY AND TERTIARY α -CARBON ATOMS

For the emulsion oxidation the per cent attack at the primary position has been calculated as the sum of the mole % of primary alcohol and hydroperoxide, the mole % of cumic acid, and one-half the mole % of the oxy-acids. Similarly, the extent of attack at the tertiary carbon has been calculated by summing the mole % of tertiary hydroperoxide, tertiary alcohol, and ketone, and one-half of the mole % of the oxy-acids. The per cent attack at the two positions in the photochemical oxidation has been based on the composition of the product as determined by reduction with lithium aluminum hydride and separation of the resulting alcohols.

DISCUSSION

The results presented in Table II indicate that within experimental error the *relative* activity of the methyl and isopropyl groups toward oxidative attack is the same in the emulsion and photochemical reactions. This, of course, is not surprising. The nature of the major proportion of the product will be determined by the identity of the propagation steps and these are the same for oxidation under the two conditions, namely,

$$\begin{array}{ccc} \mathrm{R} \cdot + \mathrm{O}_2 & \longrightarrow & \mathrm{RO}_2 \cdot \\ \mathrm{RO}_2 \cdot + & \mathrm{RH} & \longrightarrow & \mathrm{RO}_2\mathrm{H} + & \mathrm{R} \cdot , \end{array}$$

where R \cdot is either the primary or tertiary cymyl radical and RO₂H is the corresponding hydroperoxide (2). Some product may be attributed to the initiation and termination steps of the oxidation, but since the reaction chains are probably fairly long, this will constitute a very minor proportion of the total. Furthermore, the relative activity of different radicals toward the primary and tertiary carbon atoms will be approximately the same regardless of their nature. Thus, some reaction chains in the emulsion oxidation may be initiated by RO \cdot and HO \cdot radicals formed by thermal decomposition of the hydroperoxide (18). The relative activity of these radicals towards the two reaction sites, however, should correspond closely to that of the RO₂ radicals acting in the propagation step.

It is of interest to compare the results of the present study with those reported by Kooyman (11) who obtained a measure of hydrocarbon activity in radical reactions by comparing the inhibiting action of different hydrocarbons in the propagation step of the peroxide-catalyzed addition of carbon tetrachloride to olefins. He has found that the ratio of the α -methylenic activity of the isopropyl group of cumene to that of the methyl group of toluene is 4.2:1 at 91.5°C. This corresponds fairly closely to the 3.5:1 ratio for the two groups obtained at 85°C. in the present study^{*}.

As stated earlier, the isolation of cuminaldehyde from the products of the decomposition of the sodium salt of the hydroperoxide formed in a photochemical oxidation was considered by Helberger to characterize the hydroperoxide as the primary compound, III. This experimental result, confirmed in the present study, is not in conflict, however, with the fact that the oxidation product actually contains only 20% of III, the remainder being the tertiary hydroperoxide, II. It has been well established that primary hydroperoxides decompose very readily in the presence of alkali to form aldehvdes. Hock and Lang (8), for example, obtained *p*-tolualdehyde in good yield by warming p-xylyl hydroperoxide with an equivalent of alkali for a few minutes. Tertiary hydroperoxides, on the other hand, are considerably more stable toward alkali, particularly when sufficient is present to convert the hydroperoxide to its salt. Thus, Kharasch (10) has shown that in the presence of excess alkali α -cumyl hydroperoxide is decomposed only to the extent of 70% at 90°C. in six hours and the main product is 2-phenyl-2-propanol. In the present investigation the treatment of the cymyl hydroperoxide salts for 15 min. with boiling water would be expected to completely decompose the

*Kooyman has also shown that whereas the activity of m-xylene is exactly twice that of toluene the activity of o- and p-xylene is significantly greater than twice. Because of this mutual interaction of groups in ortho and para positions the relative activity of the two alkyl groups of p-cymene, as determined in the present study, is not a true measure of the activity of methyl and isopropyl groups attached to the benzene ring. This could be determined, however, from a similar study of the oxidation of m-cymene. primary component to cuminaldehyde and partially decompose the tertiary component to the tertiary alcohol.

EXPERIMENTAL*

Purification of p-Cymene

Eastman Kodak "White Label" *p*-cymene was dried over Drierite and distilled over sodium through a 30 plate column. A mid-fraction, b.p. 62.5°C. (12 mm.), $n_{\rm D}^{20}$ 1.4908, was used in the oxidation studies.

Emulsion Oxidation

Apparatus

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A train consisting of an activated charcoal tower, solid sodium hydroxide tower, back-splash trap, sulphuric acid trap, and glass wool tower was used to purify cylinder oxygen. Gas-flow rate was regulated by a needle valve and measured with a mercury flowmeter. The reaction vessel consisted of a three-neck five-liter flask provided with a fritted-glass gas dispersion tube, mercury-seal stirrer, thermometer, and condenser. The top of the condenser was connected through a dry-ice trap to a wet-test gasmeter.

Oxidation Procedure

The reaction vessel was charged with a reaction mixture of the following composition:

| water | 2000.0 gm. |
|---------------------|------------|
| <i>p</i> -cymene | 340.0 gm. |
| stearic acid | 3.0 gm. |
| sodium carbonate | 27.0 gm. |
| cymyl hydroperoxide | 0.4 gm. |

The stirred mixture was brought to the desired temperature and the oxygen flow adjusted to seven liters per hour. The oxidation was followed using an iodometric procedure (7) for hydroperoxide analysis of samples periodically removed from the reaction flask. The reaction at 85° C. was stopped when the hydroperoxide content of the cymene had reached 40% by weight. This required 35.5 hr. The reaction at 60° C. was interrupted after 197 hr. at which time the hydroperoxide concentration was 19%. Two layers separated on cooling. The aqueous layer was separated and washed with petroleum ether (b.p. $30-60^{\circ}$ C.), care being taken to retain the flocculent sodium stearate with the water. The ether washings were combined with the organic layer. The greater part of the ether was removed *in vacuo* and the residue divided into two aliquots for further treatment. The aqueous layer was acidified with dilute hydrochloric acid, the precipitated acids taken up in ethyl ether, the ether removed, and the acids separated by a chromatographic procedure.

Lithium Aluminum Hydride Reduction of Aliquot I

Aliquot I from each oxidation (three-quarters of the organic layer from the 85°C. reaction and one-half from the 60°C. reaction) was diluted with

*All melting and boiling points are corrected.

500 ml. of ether and the solution added dropwise with stirring to a 25% excess of a 2 N ethereal solution of lithium aluminum hydride. The mixture was decomposed with water followed by sufficient 10% sulphuric acid to just barely dissolve the basic aluminum salts. The ether layer was separated and washed with 10% sodium bicarbonate. The ether was removed and the product fractionated in a 35 plate column (13) using benzhydrol as the chaser. Two fractions were obtained in addition to unreacted cymene. Fraction I, b.p. 105-106°C. (12 mm.) was a mixture of 2-*p*-tolyl-2-propanol and 1-*p*-tolylethanol. Fraction II, b.p. 125.5-126.5°C. (12 mm.) was *p*-isopropylbenzyl alcohol.* A phenylurethan derivative of this fraction melted at 62.0-62.5°C., reported 62.5°C. (14).

Treatment of Aliquot II

Aliquot II of each oxidation product was added slowly to twice its volume of an ice-cooled 25% solution of sodium hydroxide. The hydroperoxide salt separated in about two hours.** It was filtered rapidly using an ice cooled. fritted-glass funnel, washed with petroleum ether and dried. The salt was crushed to a fine powder, stirred with 150 ml. of petroleum ether, filtered and again dried. This product was suspended in water and the hydroperoxide liberated by passing in carbon dioxide until a pH of 8 had been reached. The hydroperoxide was taken up in petroleum ether and the ether removed in vacuo. The colorless oily residue analyzed for 98-99% cymyl hydroperoxide. It was diluted with ether and reduced with lithium aluminum hydride using the procedure already described. Fractionation of the reduction product in the 35 plate column using benzhydrol as the chaser furnished 2-p-tolyl-2-propanol, b.p. 105-106°C. (12 mm.), n_D²⁰ 1.5174.† The yield was 93 and 91% based on the isolated hydroperoxide and 78 and 71% based on the hydroperoxide content of the original oxidation mixture for the 85 and 60°C. oxidations, respectively. There was no evidence of a p-isopropylbenzyl alcohol fraction boiling between the tertiary alcohol and the chaser.

The organic layer of the filtrate from the hydroperoxide salt filtration was separated and the petroleum ether distilled off. The residue was heated under reflux for three hours to decompose hydroperoxides and a sample was then removed for ketone analysis (16). The remainder on fractionation furnished a single fraction consisting mainly of 2-p-tolyl-2-propanol and p-methyl-acetophenone.[‡] The primary alcohol, p-isopropylbenzyl alcohol, could not be isolated at this stage. Reduction with lithium aluminum hydride of the product of this distillation followed by a fractionation of the reduction product,

* Fractionation of a synthetic mixture of these alcohols demonstrated that the primary alcohol does not form an azeotrope with the other alcohol components.

**Seeding of the alkaline mixture with a small amount of the hydroperoxide salt induced immediate precipitation. This method was used in the treatment of the 85°C. oxidation product and resulted in higher hydroperoxide recovery.

[†]The slightly high refractive index of this product was attributed to the presence of a small amount of α , p-dimethylstyrene $(n_D^{20} \ 1.5283)$ formed by dehydration of the alcohol. When the column was maintained at total reflux for a short period droplets of water appeared in the head and the refractive index of subsequent distillate increased. [†]The ketone was identified by means of its 2,4-dinitrophenylhydrazone, m.p. 259.8-260.6°C.

[‡]The ketone was identified by means of its 2,4-dinitrophenylhydrazone, m.p. 259.8-260.6°C., which gave no melting point depression when mixed with an authentic sample of this derivative. however, furnished a very small fraction boiling between the main product and the chaser. This was identified by its phenylurethan derivative as the primary alcohol.

Separation and Identification of the Carboxylic Acid Oxidation Products

The acids were separated by column partition chromatography using methanol on silicic acid as the stationary phase and benzene saturated with aqueous methanol as the mobile phase. The packing was prepared by grinding 150 gm. of Mallinckrodt A. R., 100 mesh, silicic acid with 200 ml. of methanol, 7.5 ml. of a 1% methanolic bromocresol green solution, and 2 ml. of 1 N ammonium hydroxide until a homogeneous powder was produced (15). The powder was slurried with 300 ml. of benzene and poured into 49 \times 3.5 cm. (diam.) column. Benzene, equilibrated with 90% aqueous methanol, was forced through the column to remove excess indicator and, using this solvent as eluent, 0.5 gm. of cumic acid was then passed through to remove excess ammonium hydroxide. Elution with 'equilibrated' benzene of two grams of the acid oxidation product, placed on the column in 25 ml. of this solvent, produced four distinct bands. The eluent corresponding to each band was collected and the solvent removed *in vacuo* to give separated acids in a total recovery of 95–98%.

The first band emerging from the column comprised a mixture of cumic and stearic acids, which could not be separated adequately by the above described chromatographic procedure. Recrystallization of this mixture from aqueous ethanol, however, furnished a product which gave no melting point depression when mixed with an authentic sample of cumic acid and gave a neut. equiv. of 164.7, calc. 164.2. Since care had been taken to retain precipitated sodium stearate with the aqueous layer of the oxidation product a fairly accurate correction for the stearic acid present in the first band could be made.

The second acid, recrystallized from benzene-ethanol, was *p*-acetylbenzoic acid: m.p. found 209.2-209.8°C., reported (5) 208.6-209.4°C.; neut. equiv. found 168.2, calc. 164.2; phenylhydrazone m.p. found 234-235°C., reported 234°C.

The fourth acid to pass from the column was recrystallized from ethanolbenzene and identified as p-(α -hydroxyisopropyl)benzoic acid: m.p. found 159.2—159.6°C., reported (4) 156°C.; neut. equiv. found 180.5, calc. 180.2.

The third acid after recrystallization from benzene-ethanol gave a melting point of $151.5-151.8^{\circ}$ C. Its neut. equiv. and peroxidic oxygen content agreed with the calculated values for *p*-(α -hydroperoxyisopropyl)benzoic acid: neut. equiv. 196.9, calc. 196.2; peroxidic oxygen found 16.34, 16.28, calc. 16.31%.

The hydroperoxy acid was further identified by sodium sulphide reduction to p-(α -hydroxyisopropyl)benzoic acid. The acid, 0.085 gm., was refluxed overnight with 10 ml. of water, 0.05 gm. of sodium carbonate and 0.10 gm. sodium sulphide hydrate. The product was acidified and the precipitated acids separated chromatographically by the method already described. There was obtained 0.069 gm. (88%) of p-(α -hydroxyisopropyl)benzoic acid and 0.003 gm. (4%) of p-acetylbenzoic acid.

Finally, the hydroperoxy acid was decomposed in the presence of cobalt ion. The acid, 0.150 gm., was refluxed for three hours with 45 ml. of benzene and six drops of cobalt napthenate solution (Nuodex Cobalt 6%). The product was taken up in 10% sodium carbonate, and the acids precipitated with dilute hydrochloric acid. Using crystallization and chromatographic procedures, 0.059 gm. (43%) of p-(α -hydroxyisopropyl)benzoic acid and 0.0465 gm. (37%) of p-acetylbenzoic acid was obtained.

Preparation and Properties of 2-p-Tolyl-2-propyl Hydroperoxide, II

The sodium salt of the hydroperoxide, isolated from the products of a separate 85°C. oxidation in the manner already described, was converted to the free hydroperoxide by treatment with carbon dioxide and then reprecipitated. The salt (97.4% pure) was treated with carbon dioxide and the liberated hydroperoxide extracted with petroleum ether. Removal of the ether left a colorless oily liquid which analyzed for 98.9% hydroperoxide. Distillation *in vacuo* furnished a colorless liquid: b.p. 88–91°C. (1 mm.); $n_{\rm D}^{20}$ 1.5207; d_4^{25} 1.0403; peroxidic oxygen found 19.04, 19.12%, calc. 19.25%. On the basis of the results obtained from the reduction of the hydroperoxide described above, this product was considered to be essentially pure tertiary hydroperoxide, II.

Photochemical Oxidation

Apparatus and Procedure

The apparatus was identical with that used for the emulsion oxidations except that the reactor was a two-liter flask surrounded by a box lined with aluminum foil. The box was fitted with a 100 watt bulb connected to a Variac to provide a variable heat source and across an open end was aligned an 18 in. long quartz d-c. mercury-vapor lamp. The flask was charged with 850 gm. of p-cymene, the temperature raised to 60°C., and the oxygen flow started and adjusted to seven liters per hour. After 118 hr., a hydroperoxide concentration of 5.5% by weight had been reached and the reaction was then stopped.

Lithium Aluminum Hydride Reduction

The total oxidation product was reduced with lithium aluminum hydride using the procedure already described. The reduction product was fractionally distilled using benzhydrol as the chaser. Two fractions were obtained in addition to unchanged *p*-cymene. Fraction 1, b.p. 105—106°C. (12 mm.), $n_{\rm D}^{20}$ 1.5172, wt. 34.1 gm. was 2-*p*-tolyl-2-propanol, and Fraction 2, b.p. 125.0—126.5°C. (12 mm.) $n_{\rm D}^{20}$ 1.5204, wt. 8.8 gm. was *p*-isopropylbenzyl alcohol. The total weight of 42.9 gm. compared with a theoretical yield of 42.4 gm. based on the hydroperoxide content of the oxidation product.

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