TABLE II

Attempted Isomerization of the Isomeric 1,2-Dibromocyclohexanes with Silver Bromide and Bromine

Dibromide	Before Treatment		After Treatment			
	M.p., °C.	n_D^{25}	% Recovery	M.p., °C.	n_D^{25}	I.R. spectrum
cis	10.0	1.5512	60	6.5	1.5511	All *cis*
trans	−4.5	1.5505	94	−4.5	1.5505	All *trans*

dicarboxylic acid (using reflux temperature) to which was added a sample of known *cis*-1,2-dibromocyclohexane. The product, worked up in the usual fashion, showed a melting point depression of about 30° and gave an infrared spectrum completely identical with that of a synthetic mixture made up of authentic *cis*- and *trans*-dibromides. The data could not distinguish partial isomerization from complete retention of configuration, but there could be no doubt that a very large portion of the *cis*-1,2-dibromocyclohexane survived the reaction.

cis-1,2-Cyclohexanedicarboxylic acid was also subjected to the treatment with bromine and silver bromide in anhydrous carbon tetrachloride at reflux for 12 hr. The acid was recovered quantitatively with no change in melting point indicating that no isomerization had taken place.

All infrared spectra were obtained using a Baird Associates recording spectrophotometer with a sodium chloride prism. The samples were run as pure liquid films.

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Hydrogenolysis of Acylhydroquinones

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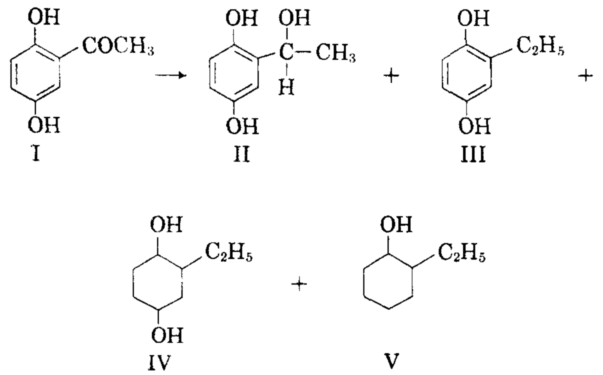
Four acylhydroquinones have been hydrogenated to the corresponding dialkylhydroquinones at 140–150° and 3000–4000 p.s.i. In the case of 2,5-dihydroxycaprylophenone, the hydrogenation either was stopped at the intermediate carbinol stage or was carried to completion, yielding *n*-octylhydroquinone, by the use of suitable operating conditions.

In an earlier work[1] when acetylhydroquinone (I) was hydrogenated using Adams' catalyst, W-6 Raney nickel, or W-7 Raney nickel catalysts at room temperature and 25–50 p.s.i., the products included 2,5-dihydroxyphenylmethylcarbinol (II), ethylhydroquinone (III), ring hydrogenated products, and possibly some of the corresponding hydrogenolysis products, such as IV and V.



The use of copper chromite-type catalysts, such as HJS-2 and Harshaw Cu-X, with proper temperature control made possible the stepwise hydrogenation at about 2000–4000 p.s.i. of acetylhydroquinone (I) to 2,5-dihydroxyphenylmethylcarbinol (II) and ethylhydroquinone (III) in excellent yields.[2]

Since the above work was completed, further examples of the hydrogenolysis reaction have been carried out, using other acylhydroquinones.

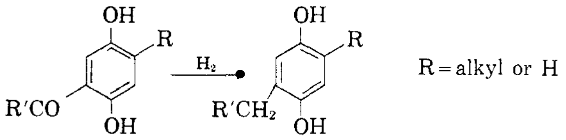


Table I summarizes the results obtained when four acylhydroquinones underwent hydrogenolysis at 140–150° and 3000 – 4000 p.s.i.

TABLE I

Hydrogenolysis of Alkylacylhydroquinones

Ketone	Product
2,5-Dihydroxy-4-methylacetophenone	2-Methyl-5-ethylhydroquinone
2,5-Dihydroxy-4-methylpalmitophenone	2-Methyl-5-hexadecylhydroquinone
2,5-Dihydroxy-4-*n*-octylcaprylophenone	2,5-Di-*n*-octylhydroquinone
2,5-Dihydroxycaprylophenone	*n*-Octylhydroquinone

2,5-Dihydroxycaprylophenone can also be hydrogenated under milder conditions to 2,5-dihydroxyphenylheptylcarbinol in low yield. While these hydrogenations require the use of medium-pressure equipment (2000–4000 p.s.i.), the reaction times are convenient, being of the order of 1–2.5 hours.

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(1) D. D. Reynolds, J. A. Cathcart, and J. L. R. Williams, *J. Org. Chem.*, **18**, 1709 (1953).

(2) J. L. R. Williams, *J. Org. Chem.*, **19**, 1205 (1954).

Others[3,4] have carried out the hydrogenolysis of acylhydroquinones using 10% palladium on charcoal at atmospheric pressure and low pressures (25–50 p.s.i.). Although the yields were good, the hydrogenolysis times were excessive, of the order of 4 to 20 hours. The advantages of the present method at 2000–4000 p.s.i. are: shorter reaction times, less noncrystallizable by-product, and complete hydrogenolysis of the ketone (less than 0.2% residual carbonyl by ultraviolet absorption analysis).

EXPERIMENTAL

Hydrogenation of 2,5-dihydroxycaprylophenone. α-(2,5-Dihydroxyphenyl)octanol-1. In a stainless-steel reactor were placed 46.7 g. (0.19 mole) of 2,5-dihydroxycaprylophenone,[5] 4 g. of copper chromite catalyst (Harshaw Cu-X-647-57-P) and sufficient ethanol to make a final volume of 150 ml. Hydrogenation at 100–106° and 3800 p.s.i. for 40 min. was carried out. Pressure drop at room temperature, 450 p.s.i.; calcd., 350 p.s.i.

The cooled reaction mixture was filtered and the ethanol evaporated under reduced pressure (water aspirator). The solid residue was recrystallized from 200 ml. of hexane and 25 ml. of ether to give 8.3 g. of α-(2,5-dihydroxyphenyl)-octanol-1, m.p., 77–78°.

Anal. Calcd. for $C_{14}H_{23}O_3$: C, 70.6; H, 9.3. Found: C, 70.1; H, 9.2.

The hexane-ether mother liquors were evaporated to dryness (yield, 34 g.) and 1 g. of the residue was recrystallized from a mixture of 15 ml. of benzene and 10 ml. of hexane to give material, m.p., 81.5–82.0°.

Anal. Calcd. for $C_{14}H_{23}O_3$: C, 70.6; H, 9.3. Found: C, 72.2; H, 9.0.

This is a mixture of carbinol and *n*-octylhydroquinone.

α-(2,5-Diacetoxyphenyl)octanol-1-acetate. A solution of 34 g. (0.142 mole) of the carbinol mixture, m.p. 81.5–82.0°, in 50 g. of acetic anhydride was allowed to stand at room temperature 48 hr. The volume was reduced to one-half the original, at reduced pressure and at 35°. After the addition of 50 g. of acetic anhydride, the reaction mixture was heated at 60° for 6 hr. Two hundred milliliters of benzene was added, and the whole extracted twice with water. The organic layer was separated and dried over anhydrous magnesium sulfate. Distillation gave 30.2 g. (62%) of 2,5-diacetoxyphenylheptylcarbinol acetate, b.p., 148° (0.2 mm.).

Anal. Calcd. for $C_{20}H_{28}O_6$: C, 66.6; H, 7.8; acetyl, 31.2. Found: C, 66.7; H, 7.8; acetyl, 31.3.

n-Octylhydroquinone. A mixture of 47.2 g. (0.2 mole) of 2,5-dihydroxycaprylophenone,[5] 4 g. of copper chromite catalyst (Harshaw Cu-X-649-57-P), and 110 ml. of absolute ethanol was hydrogenated at 103–115° and 3800 p.s.i. until the absorption of hydrogen ceased (40 min.). The temperature was raised to 150–160° (3380 p.s.i.) and maintained at that value for 1.25 hr. (Pressure drop at room temperature, 940 p.s.i.; calcd., 960 p.s.i.). Filtration and evaporation of the reaction mixture gave crude *n*-octylhydroquinone, m.p., 90–94°. Recrystallization from hexane gave material melting at 96–97°. Literature[3] m.p., 96.5–98°.

Hydrogenation of 2,5-dihydroxy-4-methylacetophenone. A mixture of 163 g. (0.78 mole) of toluhydroquinone diacetate and 330 g. (2.5 moles) of anhydrous aluminum chloride was divided into three portions. One portion was placed in a 1-l. beaker surrounded by an oil bath maintained at 125–130°. The reaction mixture was stirred vigorously until the reaction subsided. The second and third portions were added using the same procedure, after which time (5 min.) the reaction mixture was allowed to stand at 115–120° for 15 min. The reaction mixture was cooled, ground in a mortar, and poured into a rapidly stirred mixture of 300 ml. of concentrated hydrochloric acid and 4 l. of ice. After stirring for 1 hr., the solid was filtered and dissolved in 600 ml. of benzene. The solution was dried over anhydrous magnesium sulfate and evaporated to dryness under reduced pressure. The residue was stirred with 150 ml. of a 7% hydrogen chloride in methanol solution for 1 hr. The resulting solution was poured into 2 l. of ice water and the solid filtered. Recrystallization from a mixture of 100 ml. of ethanol and 300 ml. of water yielded crude 2,5-dihydroxy-4-methylacetophenone, m.p., 141.5–144.0°. Recrystallization again from 2 l. of benzene yielded 50 g. (38.5%) of pure ketone, m.p. 146–147°. Evaporation of the mother liquors to 200 ml. yielded an additional 3.8 g. of ketone.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.0; H, 6.1. Found: C, 65.3; H, 6.1.

2-Ethyl-5-methylhydroquinone. A mixture of 25 g. (0.15 mole) of 2,5-dihydroxy-4-methylacetophenone, 4 g. of copper chromite catalyst (Harshaw Cu-X-649-57-P), and 130 ml. of absolute ethanol was hydrogenated at 105–115° and 3700 p.s.i., at which temperature one molar equivalent of hydrogen was absorbed. The temperature was then maintained at 140° for 1 hr. The filtered reaction mixture was evaporated to yield a white solid, m.p. 160–164°. By recrystallization from a mixture of 200 ml. of ether and 400 ml. of benzene, there was obtained 11.7 g. of 2-ethyl-5-methylhydroquinone, m.p., 170–171°. The mother liquors were treated with Norit, and evaporated to 250 ml. Cooling in ice gave an additional 5 g. of 2-ethyl-5-methylhydroquinone, m.p. 169.5–170.5°. The total yield was 16.7 g. or 70%.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.0; H, 7.9. Found: C, 70.8; H, 8.1.

Diacetate, m.p., 114–115°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.0; H, 6.8. Found: C, 66.4; H, 6.8.

Hydrogenation of 2,5-dihydroxy-4-methylpalmitophenone. 2-Methyl-5-hexadecylhydroquinone. A mixture of 36.2 g. (0.1 mole) of 2,5-dihydroxy-4-methylpalmitophenone,[5] 4 g. of copper chromite catalyst (Harshaw Cu-X-649-57-P), and 130 ml. of absolute ethanol was treated with hydrogen at 145–155° and 3850 p.s.i. for 1.25 hr. The pressure drop at room temperature was 550 p.s.i., calcd., 480 p.s.i. A sample of the cooled material from the bomb, after drying on a porous plate for a few minutes, melted at 123–127°. The solid was dissolved in acetone and the catalyst was filtered. The acetone was evaporated, and the residue recrystallized from 250 ml. of glacial acetic acid to which there was added a small amount of zinc dust. There was obtained 29.5 g. (85%) of 2-methyl-5-hexadecylhydroquinone, m.p., 125–127°. Ten grams of the material, when recrystallized again from 100 ml. of acetic acid, gave 8 g. of pure 2-methyl-5-hexadecylhydroquinone, m.p., 126.5–127.5°. Literature[4] m.p., 127–128°.

2,5-Dihydroxy-4-n-octylcaprylophenone. A charge consisting of 15 g. (0.43 mole) of 2,5-dihydroxy-4-*n*-octylcaprylophenone,[5] 2.5 g. of copper chromite catalyst (Harshaw Cu-X-649-57-P), and absolute ethanol to give a final volume of 150 ml. was hydrogenated at 150–160° and 4200 p.s.i. during 1 hr. Pressure drop at room temperature was 260 p.s.i., calcd., 210 p.s.i.

The catalyst was removed by filtration, and the ethanol evaporated at reduced pressure to give 13.4 g. of material,

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(3) A. Loria, J. R. Thirtle, and A. Weissberger (Eastman Kodak Co.), U. S. Patent **2,728,659** (Dec. 27, 1955).

(4) J. R. Thirtle, P. W. Vittum, and A. Weissberger (Eastman Kodak Co.), U. S. Patent **2,732,300** (Jan. 24, 1956).

(5) The author is indebted to R. J. Thirtle for supplying these ketones.

m.p., 104–109°. Recrystallization from 100 ml. of cyclohexane gave 11.3 g. (79%) of 2,5-di-*n*-octylhydroquinone, m.p. 109.0–109.5°. An additional recrystallization from 80 ml. of hexane gave 8 g. of pure product, m.p. 110.5–111.5°. Literature[3] m.p. 109.5–110.5°.

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[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

Reaction of *t*-Butyl Peroxide with Acetals

LESTER P. KUHN AND CARL WELLMAN

Received January 21, 1957

The decomposition of *t*-butyl peroxide in 1,1-diethoxybutane and in 1,1-diisopropoxybutane has been studied in the liquid phase. From the ethyl acetal the major products are ethane, *t*-butyl alcohol, acetaldehyde, ethyl butyrate, ethyl *n*-butyl ether, *n*-butyraldehyde, and 4,5-diethoxyoctane. From the isopropyl acetal the corresponding isopropyl derivatives were obtained. On the basis of the products obtained and their yields a mechanism is proposed which involves the abstraction of a hydrogen atom by a *t*-butoxy radical from a carbon atom of the acetal which is adjacent to oxygen. The new radical which is thus formed decomposes to yield an alkyl radical and a carbonyl-containing compound.

$$\mathrm{R_2\dot{C}OEt} \longrightarrow \mathrm{R_2C{=}O} + \mathrm{Et}^{\cdot}$$

The object of this work was to determine the mode of reaction between alkoxy radicals and acetals. To this end, *t*-butyl peroxide was decomposed in the acetal at 120–140° at an initial concentration of 10 mole % peroxide. On the basis of the products formed a reasonable mechanism is presented which accounts for the experimental results and which is consistent with the known reactions of alkoxy radicals.

From the decomposition of *t*-butyl peroxide in 1,1-diethoxybutane a complex mixture of products was obtained which was successfully separated and analyzed by means of gas chromatography. The results are shown in Table I. The variation in yields from run to run was about ±5%.

TABLE I

PRODUCTS FROM THE DECOMPOSITION OF *t*-BUTYL PEROXIDE IN 1,1-DIETHOXYBUTANE

Compound	Yield[a] Observed	Calcd.
Methane	0.32	0.32
Ethane	1.07	1.25
Butane	0.09	0.09
Acetaldehyde	2.86	2.86
Acetone	0.32	0.32
t-Butyl alcohol	1.7	1.61
n-Butyraldehyde	0.54	0.54
Ethyl *n*-butyl ether	0.61	0.61
Ethyl butyrate	0.92	0.90
4,5-Diethoxyoctane	0.88	0.88

[a] The yield is expressed in moles per mole of peroxide decomposed.

The following reactions satisfactorily account for the products and the observed yields:

$$\underset{1}{(t\text{-BuO})_2} \longrightarrow \underset{2}{2t\text{-BuO}^{\cdot}}$$

$$\underset{0.9}{t\text{-BuO}^{\cdot}} + \underset{0.9}{\mathrm{C_3H_7CH(OC_2H_5)_2}} \longrightarrow \underset{0.9}{t\text{-BuOH}} + \underset{0.9}{\mathrm{C_2H_7\dot{C}(OC_2H_5)_2}}\ \ \text{I}$$

$$\underset{0.9}{\mathrm{C_3H_7C(OC_2H_5)_2}} \longrightarrow \underset{0.9}{\mathrm{C_3H_7COOC_2H_5}} + \underset{0.9}{\mathrm{C_2H_5}^{\cdot}}$$

$$\underset{0.72}{t\text{-BuO}^{\cdot}} + \underset{0.72}{\mathrm{C_3H_7CH(OC_2H_5)_2}} \longrightarrow \underset{0.72}{t\text{-BuOH}} + \underset{0.72}{\mathrm{C_3H_7CH(OC_2H_5)O\dot{C}HCH_3}}\ \ \text{II}$$

$$\underset{1.25}{\mathrm{C_2H_5}^{\cdot}} + \underset{1.25}{\mathrm{C_3H_7CH(OC_2H_5)_2}} \longrightarrow \underset{1.25}{\mathrm{C_2H_6}} + \underset{1.25}{\mathrm{C_3H_7CH(OC_2H_5)O\dot{C}HCH_3}}\ \ \text{II}$$

$$\underset{2.9}{\mathrm{C_3H_7CH(OC_2H_5)O\dot{C}HCH_3}} \longrightarrow \underset{2.9}{\mathrm{CH_3CHO}} + \underset{2.9}{\mathrm{C_3H_7CH(OC_2H_5)}^{\cdot}}\ \ \text{III}$$

$$\underset{.54}{\mathrm{C_3H_7CH(OC_2H_5)}^{\cdot}} \longrightarrow \underset{.54}{\mathrm{C_3H_7CHO}} + \underset{.54}{\mathrm{C_2H_5}^{\cdot}}$$

$$\underset{0.61}{\mathrm{C_3H_7CH(OC_2H_5)}^{\cdot}} + \underset{0.61}{\mathrm{C_3H_7CH(OC_2H_5)_2}} \longrightarrow \underset{0.61}{\mathrm{C_3H_7CH_2OC_2H_5}} + \underset{0.61}{\mathrm{C_3H_7CH(OC_2H_5)O\dot{C}HCH_3}}$$

$$\underset{1.76}{2\mathrm{C_3H_7CH(OC_2H_5)}^{\cdot}} \longrightarrow \underset{0.88}{\mathrm{C_3H_7CH(OC_2H_5)CH(OC_2H_5)C_3H_7}}$$

$$\underset{0.32}{t\text{-BuO}^{\cdot}} \longrightarrow \underset{0.32}{\mathrm{CH_3COCH_3}} + \underset{0.32}{\mathrm{CH_3}^{\cdot}}$$

$$\underset{0.32}{\mathrm{CH_3}^{\cdot}} + \underset{0.32}{\mathrm{C_3H_7CH(OC_2H_5)_2}} \longrightarrow \underset{0.32}{\mathrm{CH_4}} + \underset{0.32}{\mathrm{C_3H_7CH(OC_2H_5)O\dot{C}HCH_3}}$$

$$\underset{0.18}{2\mathrm{C_2H_5}^{\cdot}} \longrightarrow \underset{0.09}{\mathrm{C_4H_{10}}}$$

The arabic numbers under each reactant and product were so chosen that the yield of each product would be as close as possible to the yield observed and that each unstable intermediate formed in a particular step would be completely consumed in a subsequent step. The calculated yield of products