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THE PREPARATION OF VINYLHYDROQUINONE DIACETATE

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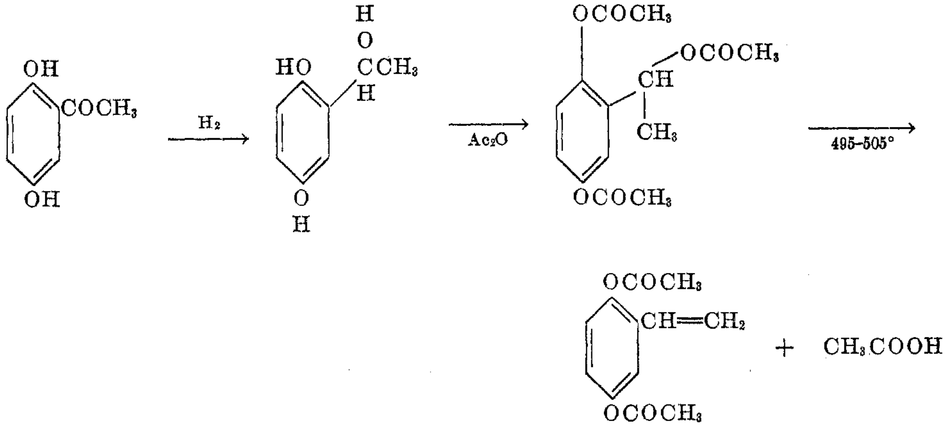
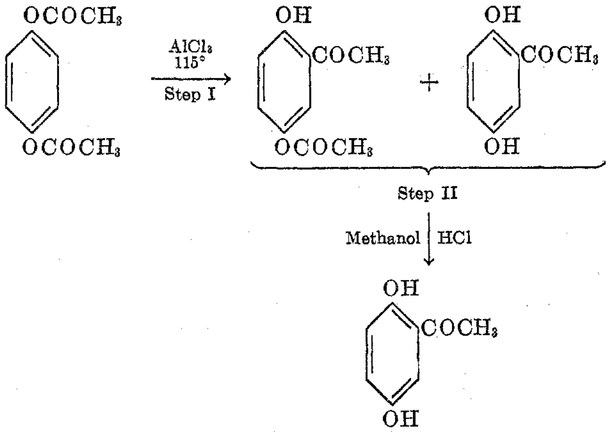
Vinylhydroquinone and polyvinylhydroquinone have been described by Updegraff and Cassidy (1). The monomer was prepared by decarboxylating 2,5-dihydroxycinnamic acid. A major difficulty not normally present in the usual polymerization is encountered in the polymerization of vinylhydroquinone, since it represents a reducing agent of the type often employed to inhibit polymerization of unsaturated organic compounds. In order to have a more easily polymerizable form of vinylhydroquinone, it was decided to synthesize vinylhydroquinone diacetate.

Acetylhydroquinone was hydrogenated to 2,5-dihydroxyphenylmethylcarbinol. The 2,5-dihydroxyphenylmethylcarbinol was then converted to the corresponding triacetate which, in turn, was pyrolyzed over glass beads at 495–505° to yield hydroquinone diacetate.

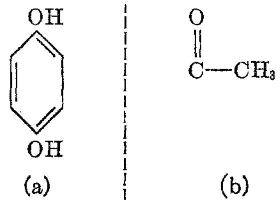


A number of methods for the preparation of acetylhydroquinone have been reported in the literature (2–12). The published methods (8, 10) which are the most useful involve a Fries rearrangement of hydroquinone diacetate. We found it difficult to reproduce the yields reported in *Organic Syntheses* (10). Moreover, acetylhydroquinone is described therein as silky green needles which melt at 202–203°, whereas earlier procedures describe it as a yellow compound. We have found that acetylhydroquinone is a bright yellow compound melting at 205–206°. The preferred procedure involves two steps.



Although two steps are involved, it is no more time-consuming than the method described in *Organic Syntheses* (10). The present method possesses the advantages that it is easily reproducible, the yields are high, and a purer product is obtained, since in Step II any unconverted starting material is removed as water-soluble hydroquinone.

Since in the systems present in acetylhydroquinone there exists a composite of acetophenone and hydroquinone, it was decided to investigate the ease of



hydrogenation of the hydroquinone system (a) and the ketone system (b).

Adkins and Billica (13) reported the use of W-6 Raney nickel for hydrogenation of hydroquinone to cyclohexane-1,4-diol and acetophenone to phenylmethylcarbinol under similar conditions, the data for which are shown in Table I.

W-7 Raney nickel (13) is more readily prepared than W-6; therefore, during the present work a similar series of hydrogenations was carried out with W-7 catalyst. Table II below summarizes the reaction times for various catalyst quantities when 11 g. of hydroquinone was hydrogenated to cyclohexane-1,4-diol at 50 p.s.i. and room temperature (25°).

The alkaline W-7 catalyst, therefore, promotes more rapid nuclear hydrogenation. Under similar conditions, 36 g. (0.3 mole) of acetophenone was hydrogenated to phenylmethylcarbinol in the presence of 12 g. of W-7 during 65 minutes. Figure 1 summarizes the data obtained when acetylhydroquinone was hydrogenated at room temperature in the presence of W-6 catalyst of two different concentrations. Figure 2 summarizes the results with W-7 catalyst and Raney cobalt under similar conditions.

Adams' catalyst (platinum oxide) was found to be a satisfactory, but less specific, catalyst for the conversion of acetylhydroquinone to 2,5-dihydroxyphenylmethylcarbinol at low pressures (Curve *A*, Fig. 3). However, to hydrogenate 0.3 mole of acetylhydroquinone within 7 hrs. (Curve *A*, Fig. 3), it was necessary to use 3 g. of catalyst (compare Curve *D*, Fig. 3, in which 1 g. of catalyst was used). When acetic acid was used as a promoter, a more rapid but still unspecific hydrogenation took place (Curve *B*, Fig. 3). It is evident from Curves *A* and *B* that secondary hydrogenations were taking place, since the curves do not flatten after the absorption of the theoretical amount of hydrogen as when W-6 Raney nickel (13) is used (Curve *C*, Fig. 3). With W-6 or W-7 Raney nickel, the hydrogenation can be completed in a relatively short time.

TABLE I

HYDROGENATIONS USING W-6 RANEY NICKEL

W-6 CATALYST, g.	STARTING MATERIAL	TIME
2.0	Acetophenone	22 min.
2.0	Hydroquinone	36 hr.
9.0	Hydroquinone	8 hr.

TABLE II

HYDROGENATION OF HYDROQUINONE

CATALYST	WT. OF CATALYST, g.	TIME, min.
W-6	20	318
W-7	11	165
W-7	33	27

Preliminary attempts to hydrogenate acetylhydroquinone to 2,5-dihydroxyphenylmethylcarbinol were unsuccessful when copper chromite was used at 125–140° and 2500 p.s.i. Ethyl hydroquinone was the product. This result is in accord with the observations of Nightingale and Radford (14), who found that "when a phenolic group is *ortho* or *para* to the carbonyl group of an aromatic aldehyde or ketone, the carbinol group is reduced to the methylene group at the temperature at which the nonphenolic aldehydes and ketones are reduced to the carbinols." In the present work, however, it was found that good yields of the carbinol could be obtained if the hydrogenation was conducted at 100–115°. In all experiments, 2,5-dihydroxyphenylmethylcarbinol was converted without isolation to 2,5-diacetoxyphenylmethylcarbinol acetate, since the former could not be crystallized, nor could it be distilled without decomposition. Unsuccessful attempts to use either aluminum isopropoxide or lithium aluminum hydride were attributed to the formation of insoluble complexes during chemical reduction which terminated the reaction.

The hydrogenation of acetylhydroquinone diacetate does not follow the same pattern with respect to catalysts as does that of acetylhydroquinone. W-6

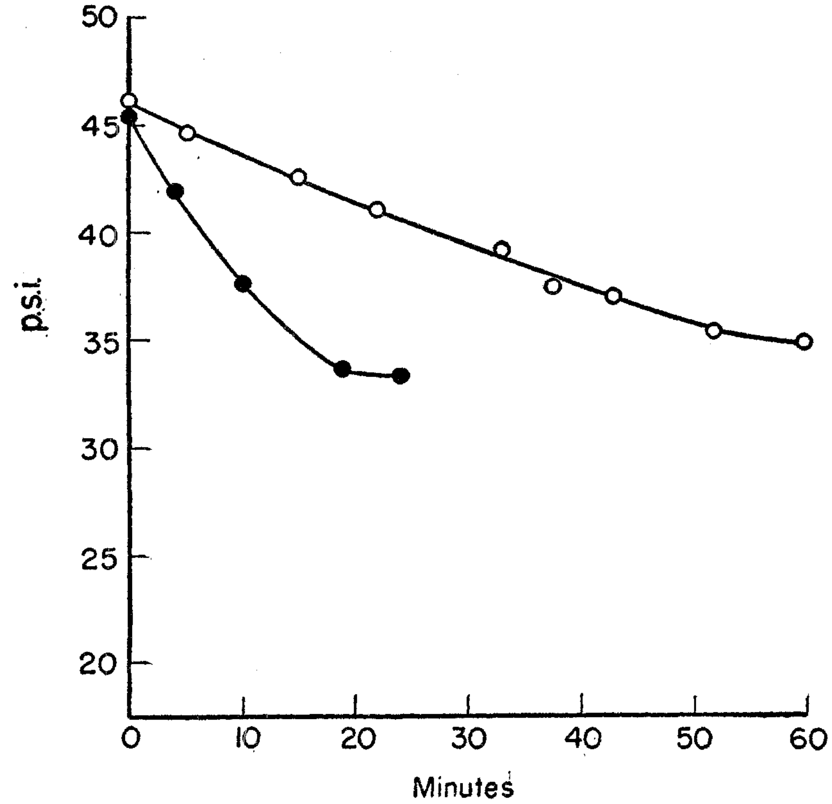


FIG. 1. ACETYLHYDROQUINONE, 18 g.: ●, W-6 Raney nickel, 10 g.; ○, W-6 Raney nickel, 5g.

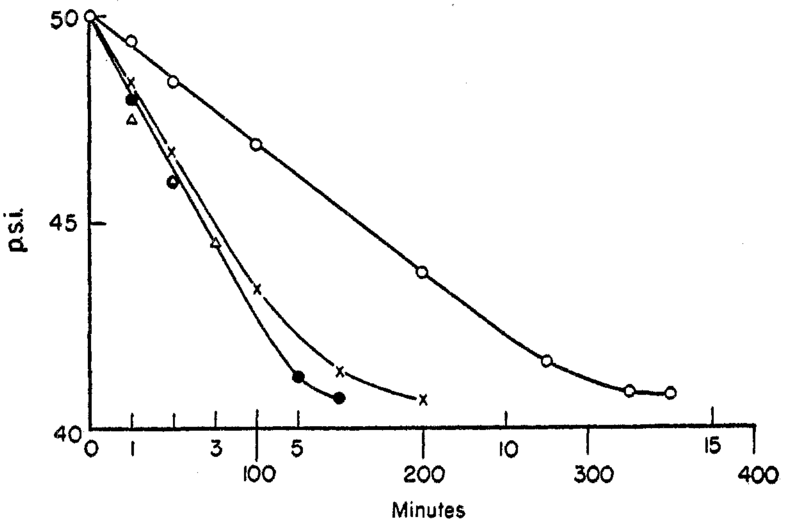


FIG. 2. ACETYLHYDROQUINONE, 14.2 g.: ●, W-7 Raney nickel, 28.4 g.; ×, W-7 Raney nickel, 14.2 g.; ○, W-7 Raney nickel, 7.1 g.; △, Raney cobalt, 21.3 g.; △, lower scale at 300 minutes was 34 p.s.i.

Raney nickel, which was among the most effective low-pressure catalysts for reduction of acetylhydroquinone, produces no reduction of the diacetate under similar conditions. Copper chromite at 150° and 2500 p.s.i. in ethanol solution caused only deacetylation. There was no reaction in dioxane. Adams' catalyst, however, gave a smooth hydrogenation of acetylhydroquinone diacetate to 2,5-diacetoxyphenylmethylcarbinol.

Pyrolysis of 2,5-diacetoxyphenylmethylcarbinol acetate was carried out in the vapor phase over glass beads at 495–505°. Lower or higher temperatures gave lower yields of vinylhydroquinone diacetate.

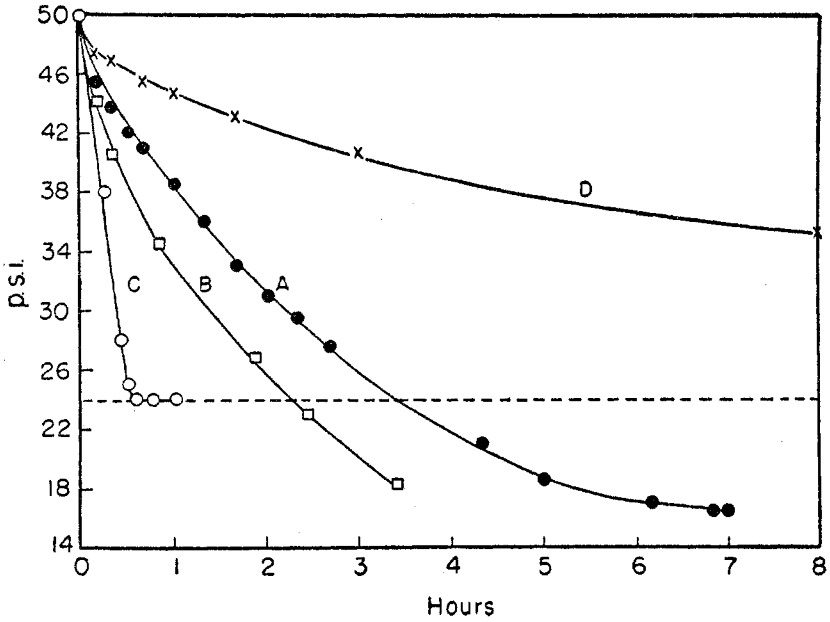


FIG. 3. ACETYLHYDROQUINONE, 45.6 g.; ×, Adams' catalyst, 1 g.; ●, Adams' catalyst, 3 g.; □, Adams' catalyst, 1 g., 2 drops glacial acetic acid; ⊙, W-6 Raney nickel, 10 g.

EXPERIMENTAL

Acetylhydroquinone. Hydroquinone diacetate (200 g., 1.23 moles), ground to 20 mesh, was mixed thoroughly with 400 g. (3.0 moles) of anhydrous aluminum chloride. One third of the mixture was added to a 1-l. beaker suspended in an oil-bath maintained at 115–120°. After the initial reaction had begun (2–4 minutes), the mixture was stirred vigorously with a glass rod until the reaction subsided. A second one-third portion was added, and the rapid stirring was repeated. The last portion was added after the reaction had subsided. The reaction mixture was then stirred for about 10 minutes. Heating with periodic stirring was then continued for 20 minutes, after which time the cooled reaction mixture was ground in a mortar and then added, with stirring, to a mixture of 4 l. of crushed ice and 200 ml. of concentrated hydrochloric acid. The resulting slurry was stirred for one-half hour, after which time the solid was filtered and washed with 1 l. of cold water. The weight of dried product, m.p. 80–85°, consisting predominantly of acetylhydroquinone monoacetate, together with some acetylhydroquinone and a trace of unchanged hydroquinone diacetate, was 185 g. This crude product was stirred for 1 hour with 375 g. of a 5% solution of hydrogen chloride in methanol. The resulting solution was poured, with stirring, into 2 l. of an ice-water mixture, the solid was filtered, and washed with 1 l. of cold water. The weight of dry acetylhydroquinone melting at 203–204° was 117 g. (75% yield). Recrystallization from ethanol and treatment with Norit gave pure material; m.p. 205–206°.

Hydrogenation of acetylhydroquinone at low pressures: 2,5-diacetoxyphenylmethylcarbinol acetate. A mixture of 45.6 g. (0.3 mole) of acetylhydroquinone and 200 ml. of ethanol was hydrogenated at low pressures in a standard Parr low-pressure apparatus using 3.0 g of Adams' catalyst. The hydrogenation pressure was 50 p.s.i. An approximately 1.0 *molar* equivalent of hydrogen was absorbed during 315 minutes. 2,5-Dihydroxyphenylmethylcarbinol was not isolated but was converted directly to 2,5-diacetoxyphenylmethylcarbinol acetate as follows: The catalyst was filtered off and the ethanol was evaporated at 60° under reduced pressure. After the addition of 200 ml. of acetic anhydride and 0.5 ml. of pyridine, the reaction mixture was allowed to stand at room temperature for 18 hours. The ethyl acetate and acetic acid formed were removed at 35–40° under reduced pressure. The concentrate was heated with 100 ml. of acetic anhydride at 60° for three hours, cooled, and washed with two 200-ml. portions of water. After the addition of an equal volume of benzene, the organic material was separated, dried over magnesium sulfate, and distilled to yield 73 g. (87.5% yield) of 2,5-diacetoxyphenylmethylcarbinol acetate; b.p. 130° (0.3 mm.); n_D^{25} 1.4942.

Hydrogenation of acetylhydroquinone at high pressures: 2,5-diacetoxyphenylmethylcarbinol acetate. In a stainless-steel rocking-type reactor there were placed 41 g. (0.27 mole) of acetylhydroquinone, 120 ml. of absolute ethanol, and 4 g. of copper chromite catalyst (Harshaw Cu-x-649-57P). The reactor was pressurized with hydrogen to 3000 p.s.i. at room temperature, after which the temperature was raised to 105°, whereupon 0.3 mole of hydrogen was absorbed. Careful control of temperature was required, since further hydrogen is absorbed in the range 120–140° to yield not the carbinol but ethylhydroquinone. The reaction mixture was worked up as described above for low-pressure hydrogenation to yield 65 g. (86% yield) of 2,5-diacetoxyphenylmethylcarbinol acetate; b.p. 124–130° (0.3 mm.); n_D^{25} 1.4968.

Anal. Calc'd for $C_{14}H_{16}O_6$: C, 64.8; H, 6.4.

Found: C, 64.5; H, 6.3.

Hydrogenation of acetylhydroquinone diacetate: 2,5-diacetoxyphenylmethylcarbinol acetate. Acetylhydroquinone diacetate (70.8 g., 0.3 mole) was mixed with 200 ml. of methanol containing 1 g. of platinum oxide catalyst. One molecular equivalent of hydrogen was absorbed in 2–3 hours. The catalyst was removed, and the methanol distilled under a vacuum. The clear, sirupy 2,5-diacetoxyphenylmethylcarbinol from two such runs was acetylated with a mixture of 500 ml. of acetic anhydride and 10 drops of concentrated sulfuric acid. After 15 hours at room temperature, the acetic acid and acetic anhydride were removed under reduced pressure by means of a 50°-bath. Chloroform, 500 ml., was added, and the solution washed with 500 ml. of water. The organic layer was dried over calcium chloride and was distilled to yield 116 g. (69%) of 2,5-diacetoxyphenylmethylcarbinol acetate; b.p. 134° (0.2 mm.); n_D^{25} 1.4971.

2,5-Diacetoxyphenylmethylcarbinol. Acetylhydroquinone diacetate (70.8 g., 0.3 mole) was mixed with 200 ml. of methanol containing 1 g. of platinum oxide catalyst. One molar equivalent of hydrogen was absorbed in 2.5 hours. Two such runs were combined, the catalyst was removed, and the resulting methanol solution containing the 2,5-diacetoxyphenylmethylcarbinol was evaporated at reduced pressure. Unreduced starting material (26 g.), m.p. 68–70°, crystallized and was separated. The filtrate was evaporated at reduced pressure and 65 g. of product (m.p. about 90°) crystallized. Recrystallization from isopropyl ether gave a product of m.p. 106–107°. The mother liquors were not worked up further.

Anal. Calc'd for $C_{12}H_{14}O_5$: C, 60.5; H, 5.9; Active H, 1.00.

Found: C, 60.5; H, 6.0; Active H, 1.01.

Vinylhydroquinone diacetate. A mixture of 60 g. of 2,5-diacetoxyphenylmethylcarbinol acetate and 60 g. of thiophene-free benzene was passed dropwise during 1.75 hours through a 25-mm O.D. Pyrex tube packed for a distance of 76 cm. with 6 × 6 mm. Raschig rings (Pyrex) and was heated to 495–505° with an electric furnace. The pyrolyzate was swept through the tube with a 100 cc. per minute dry nitrogen stream and was collected in a suction flask cooled in a Dry Ice-carbon tetrachloride-chloroform bath. The reaction product was washed with two 100-ml. portions of water after the addition of an equal volume of benzene. After the addition of a trace of picric acid, the organic material was dried over magnesium sulfate and distilled. The benzene was distilled at the water pump using a 35–40° water-bath, and the residue was distilled to yield 29 g. of material; m.p. 49–50° (porous plate); b.p. 98–106° (0.15 mm.). Recrystallization from a mixture of 30 g. of ethyl ether and 100 g. of hexane yielded 20 g. of vinylhydroquinone diacetate; m.p. 50.5–51.5°.

Anal. Calc'd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.50.
Found: C, 65.30; H, 5.50.

Dibromide: m.p. 89–90°.

Anal. Calc'd for $C_{12}H_{12}Br_2O_4$: C, 37.90; H, 3.14; Br, 42.0.
Found: C, 37.90; H, 3.20; Br, 40.9.

SUMMARY

Vinylhydroquinone diacetate has been synthesized from acetylhydroquinone. Hydrogenation of acetylhydroquinone to 2,5-dihydroxyphenylmethylcarbinol has been carried out using W-7 Raney nickel, W-6 Raney nickel, and Adams' catalyst at low pressures and with copper chromite at high pressures. Acetylhydroquinone diacetate has been hydrogenated to 2,5-dihydroxyphenylmethylcarbinol using Adams' catalyst at low pressures. 2,5-Diacetoxyphenylmethylcarbinol acetate was pyrolyzed to give vinylhydroquinone diacetate.

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