[Contribution from the School of Chemistry of the University of Minnesota]

DUROQUINONE AND SOME DERIVATIVES OF DURENE

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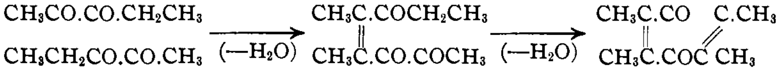
Duroquinone, tetramethyl-*p*-benzoquinone, has been made in three ways. v. Pechmann[1] found that the aliphatic α-diketones, with alkali, underwent a condensation leading to ring structures, and if the diketone is 2,3-diketopentane (acetyl propionyl), duroquinone is obtained in a yield of about 10%.



$$\begin{array}{l} CH_3CO.CO.CH_2CH_3 \\ \\ CH_3CH_2CO.CO.CH_3 \end{array} \xrightarrow[(-H_2O)]{} \begin{array}{l} CH_3C.COCH_2CH_3 \\ \quad\ \ \| \\ CH_3C.CO.COCH_3 \end{array} \xrightarrow[(-H_2O)]{} \begin{array}{l} CH_3C.CO\quad C.CH_3 \\ \quad\ \ \| \qquad\ \ /\!\!/ \\ CH_3C.COC\,CH_3 \end{array}$$

Acetyl propionyl Duroquinone

Favorsky's method[2] is essentially the same as that of v. Pechmann; he used the α,α'-dihalogenated ketones together with potassium carbonate. Thus, $2CH_3CH_2CCl_2COCH_3$ ⟶ acetyl propionyl ⟶ duroquinone. These two syntheses are interesting theoretically, but of no value for preparative purposes because the starting materials are altogether too costly and the reactions are complicated by the formation of by-products and tars, which constitute about 90% of the reaction product.

Nef,[3] who was the first to make duroquinone, prepared it by nitrating durene, reducing the dinitrodurene so formed to diaminodurene, and then oxidizing the diamine to the quinone. Nef does not mention the yield of duroquinone, but his yield of dinitrodurene was only 50% and his reduction was carried out upon 3-gram lots. Moreover, the entire process was complicated by a number of unnecessary steps, which reduced the yield of quinone considerably. However, Nef's method was the most promising of those in the literature; and, given a supply of durene, it seemed to us that a study of each of the steps in his synthesis, using larger amounts of materials, might enable us to improve the yields considerably. This expectation has been realized.

Dinitrodurene.—The nitration of durene has been carried out by a number of investigators.[3,4] Most of the experiments were carried out on very small quantities of durene, and Nef, and Rugheimer and Hankel used impure durene as the starting material. Our procedure, which is a modification of Willstätter's method of nitration, gives an average yield of over 70% and is as follows.

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[1] v. Pechmann, *Ber.*, **21,** 1420 (1888).

[2] Favorsky, *J. prakt. Chem.*, N. F., **51,** 533 (1895).

[3] Nef, (a) *Ber.*, **18,** 2806 (1885); (b) *Ann.*, **237,** 5 (1887).

[4] (a) Jannasch and Fittig, *Z. Chem.*, **6,** 162 (1870). (b) Cain, *Ber.*, **28,** 967 (1895). (c) Rugheimer and Hankel, *Ber.*, **29,** 2172 (1896). (d) Willstätter and Kubli, *Ber.*, **42,** 4151 (1909).

Thirteen and four-tenths g. (0.1 mole) of durene, dissolved in 75–100 cc. of chloroform, is floated over 50–75 cc. of concd. sulfuric acid in a liter beaker. The mixture is cooled by surrounding the beaker with ice, and 16 g. of fuming nitric acid (d., 1.5) is added drop by drop from a funnel while the mixture is rapidly stirred mechanically. The nitration requires from 10 to 15 minutes, the nitric acid being added just rapidly enough so that no excessive loss of chloroform results. The mixture is allowed to stand for a minute and then the black sulfuric acid layer is immediately separated, and the chloroform solution of the nitrodurene is run into an aqueous solution of sodium carbonate. Four portions of durene are thus nitrated in about an hour. The combined chloroform solutions of nitrodurene are extracted with water until nearly colorless. The sulfuric acid layer is extracted once with chloroform and rejected, as no appreciable quantity of nitrodurene is dissolved in it. The chloroform solutions are combined, washed with sodium carbonate solution until free from acid, dried with calcium chloride, filtered and evaporated. Nitrodurene remains almost pure white. One or two crystallizations from alcohol gives a snow-white product; m. p., 207–208°. It is important that the chloroform layer be run into the carbonate solution as soon as possible, for continued standing while acidic leads to the formation of considerable amounts of red, tarry material and this renders the purification of the nitro compound much more difficult. Excess of nitric acid is undesirable, for it cuts down the yield, while pure durene is absolutely essential for good results. It should be recrystallized from methyl or ethyl alcohol until the melting point is 79–80°.

One run, in which durene melting at 69–70° was nitrated, gave a yield of 57% of the calculated amount of nitrodurene while, with pure durene melting at 79–80°, one run of four nitrations gave a yield of 80 g. of nitrodurene, or 88%. Several other runs averaged 84% of the calculated yield, while the yield for over 40 nitrations was 72–74%. Using the directions given above, the average yield is over 80%. It is better to nitrate in small amounts, for a high yield and pure product depend upon not allowing the reaction mixture to remain in contact with the nitric acid very long. The strength of the nitric acid is of importance although this does not have as much effect as the purity of the durene. To obtain the best results the acid should have a density of about 1.5.

In the nitration of durene, no mononitrodurene is ever obtained. The nitration gives either the dinitro derivative, or unchanged material, or oxidation products.

Reduction of Dinitrodurene.—Nef[3b] reduced dinitrodurene with zinc and dil. acetic acid, precipitating the zinc with hydrogen sulfide afterward. Rugheimer and Hankel[4c] reduced it (impure) with stannous chloride, hydrochloric acid and alcohol, separating the product as the insoluble tin chloride double compound and liberating the amine from this by means of alkali. The diamine crystallizes from hot water in needles; m. p., 149°.[5] Solutions of it are easily oxidized by atmospheric oxygen.

Diacetyl Derivative.—The diamine, made from the tin salt by Rugheimer's procedure, was covered with acetic anhydride, warmed until completely dissolved and then treated with a drop of concd. sulfuric acid.

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[5] See also Ref. 4 b, p. 968.

A vigorous reaction took place, with the formation of a white precipitate. After the reaction was over, the mixture was cooled, poured into water, and the solution neutralized with sodium carbonate. The white precipitate was filtered, washed with alcohol and ether and dried. It is a fine, white powder, very insoluble in the common solvents and very stable. Sulfuric acid in concentrations of 50 to 90% has no effect on it, nor is it hydrolyzed by dilute or concentrated alkalies. The melting point is very high—above 310°, but the substance sinters and turns brown around 300°.

Anal. Calcd. for $C_{14}H_{20}O_2N_2$: N, 11.29. Found: 11.30, 11.36.

We found that for the preparation of duroquinone, it was entirely unnecessary to isolate the diamine, as the tin chloride double salt which precipitates completely from the reaction mixture can be converted directly to the quinone. Moreover, the reduction gives an excellent yield if pure dinitrodurene is used.

Ninety g. of dinitrodurene is dissolved in 800–1000 cc. of boiling glacial acetic acid in a large flask (8 or 10 liters); 700 g. of stannous chloride dissolved in 800 cc. of concd. hydrochloric acid is heated to boiling and rapidly poured into the boiling solution of nitrodurene. The reaction is over in a few minutes, during which the contents boil up and practically fill the flask. On cooling, the tin salt of diaminodurene separates out quantitatively. This is filtered and washed with a small amount of alcohol, followed by ether. The filtrates from this tin salt contain very little organic material, and may be discarded. The tin salt of the diamine crystallizes from the acetic-acid–hydrochloric-acid reaction mixture in glistening plates, almost colorless. It was analyzed directly after washing with alcohol and ether, and drying. The composition is $2C_{10}H_{12}(NH_2.HCl)_2 + SnCl_4$. In one experiment, 18 g. of dinitrodurene gave 34 g. of the tin salt, a yield of 85%. The yield is often better than this.

Anal. Calcd. for $C_{20}H_{36}N_4Cl_8Sn$ (735): N, 7.6. Found: 7.40, 7.24.

Oxidation of the Diamine.—The double salt is directly oxidized by suspending it in concentrated aqueous ferric chloride containing a little hydrochloric acid and allowing it to stand overnight. The quinone forms a thick, yellow precipitate which is filtered as dry as possible and then dissolved in benzene. The benzene is dried with calcium chloride, filtered and distilled. Practically pure duroquinone remains, which on one crystallization from alcohol melts at 111°. From 90 g. of nitrodurene 55 g. of duroquinone is obtained, a yield of 84%. In no case was the yield less than 84% and in many cases it was 90% of the calculated amount. The average yield for twelve preparations was 85%, based on the nitrodurene, which means that the oxidation of the tin salt is practically quantitative. Duroquinone crystallizes in yellow needles from ligroin or alcohol, m. p. 111°, and is readily soluble in benzene (with absorption of heat), chloroform, ether and acetone. It is volatile with steam, sublimes below its melting point and gives the weak but characteristic quinone odor.

Active reducing agents convert the quinone to the hydroquinone. There is considerable divergence as to the melting point of this substance. Nef[3] reported 210°; Rugheimer and Hankel[4c] reported 210–224°; v. Pechmann[1] reported 220°; and Conant and Fieser[6] reported 226–227°. However,

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[6] Conant and Fieser, THIS JOURNAL, **45**, 2200 (1923).

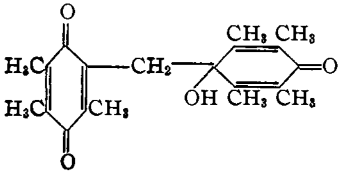
if carefully recrystallized, it melts at 233°, but sinters slightly about 220°. The diacetyl derivative was prepared by dissolving the hydroquinone in acetic anhydride, adding a drop or two of concd. sulfuric acid and refluxing for a few hours. On decomposing the mixture with alcohol and adding water, the diacetate precipitates out in long, white needles, m. p. 207° after recrystallization from alcohol.

Anal. Calcd. for $C_{14}H_{18}O_4$: H, 7.2; C, 67.2. Found: H, 7.18; C, 67.2.

Bromine reacts with the quinone when dissolved in acetone and treated with an excess of the halogen. The product consists of very faintly yellow crystals which on recrystallizing from alcohol melt at 73-74°.

Anal. Calcd. for $C_{10}H_{12}O_2Br_2$: Br, 49.4; for $C_{10}H_{12}O_2Br_4$: Br, 66.1. Found: 50.14.

In the presence of alcoholic alkali, the quinone undergoes a peculiar condensation forming an orange compound, m. p. 207°, and difficultly soluble in all common solvents. v. Pechmann[7] noticed the formation of this compound, but did not investigate it. Rugheimer and Hankel,[8] who examined this substance in some detail, found it to have the same composition as duroquinone, but a molecular weight twice as great. The presence of an hydroxyl group was proved by the formation of acetyl, propionyl, benzoyl, methyl and ethyl derivatives. On heating, duroquinone sublimes from the substance. Because of these facts, they named it "diduroquinone" and assigned this structure to it.



This structure is probably not correct; for one thing, it does not account for the fact that diduroquinone is orange, while the acetyl and other derivatives of it, if they are carefully purified, are practically colorless. We hope to investigate this compound more fully in the near future.

Summary

1. The preparation of duroquinone, and some other derivatives of durene, is discussed. The yield of duroquinone, based on the durene used, averages 67-70%.

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[7] v. Pechmann, *Ber.*, **22,** 2115 (1889).

[8] Ref. 4c, p. 2176.