## Experimental

The apparatus and general technique was that described by Zerewitinoff,[2] except that *n*-butyl ether was used as the medium for methylmagnesium iodide in all but one of the determinations. Xylene was used in some of the analyses as a solvent for the complexes with trinitrobenzene because of their low solubility in *n*-butyl ether. In each determination the amount of gas evolved by the reaction at room temperature was first determined, and then the reaction mixture was heated to 70° for fifteen minutes, after which it was cooled to room temperature for the second value.

## Summary

The complexes of *p*-amino-azobenzene and anthranilic acid with trinitrobenzene have been shown to give higher active hydrogen values than those reported by Zerewitinoff. These abnormal results are due to the interfering effect of the nitro and azo groups.

AMES, IOWA

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

# THE REACTION BETWEEN DUROQUINONE AND THE GRIGNARD REAGENTS[1]

BY LEE IRVIN SMITH AND H. MARJORIE CRAWFORD

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## Introduction and Historical Review. Statement of the Problem

In the first paper of this series[2] it was shown that the reaction between sodium malonic esters and duroquinone is not a simple addition reaction but is accompanied by oxidation leading to a product in which the malonic ester residue is linked by a double bond to what was originally one of the methyl groups of the quinone. This reaction involves the removal of both methylene hydrogen atoms of the malonic ester and both these hydrogen atoms are necessary in order for the reaction to take place.

In order to obtain more information concerning the addition of metallic derivatives to duroquinone, we have used in the present work a Grignard reagent. These reagents differ from sodium malonic ester in possessing no active "methylene" hydrogen atoms, and yet they have the advantage, in common with sodium malonic esters, of adding to carbonyl systems to give metallic derivatives which can be readily manipulated. By using the Grignard reagents we hoped to avoid the complicated oxidation reaction which accompanies the addition of sodium malonic ester and to

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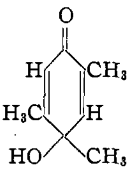
[1] Abstracted from a thesis by H. Marjorie Crawford, presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Smith and Dobrovolny, THIS JOURNAL, **48**, 1693 (1926).

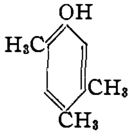
obtain products which would throw some light upon the mechanism of this malonic ester addition.

A review of the literature[3] shows that quinones may be divided into two classes: (a) quinones (such as anthraquinone) which can undergo only 1:2 addition at the carbonyl group. Only in this case is the reaction with a Grignard reagent a clean-cut one, and good yields of the mono- or di-addition product result depending upon the relative amounts of reagents used. (b) Quinones (such as *p*-xyloquinone and $\alpha$-naphthoquinone) which can undergo 1:2, 1:4 or 1:6 addition, or a combination of them. In this case the reaction becomes quite complex and leads to a large number of products. Some of these products are solids, but the yield of crystallizable solids is always low and by far the largest amount of material turns up as tars and an uncrystallizable oil, the nature of which no one, so far, has been able to determine.

The most thorough piece of work in this field is undoubtedly that of Bamberger and Blangey.[3g] Adding methylmagnesium iodide to *p*-xyloquinone, these investigators isolated from the reaction mixture six solid addition products, namely, pseudocumoquinol (A); its reduction product, pseudocumenol, (B); dihydrotrimethylquinone, (C); tetramethylcyclohexanedione, (D); prehnitol, (E) and *p*-dixyloquinol momomethyl ether, (F).



(A)



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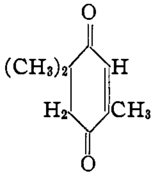

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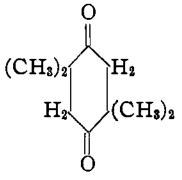

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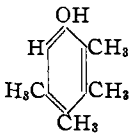
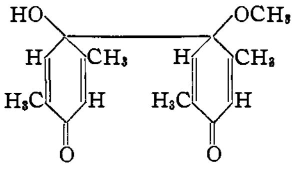


(E)



(F)

Of these six compounds, three (A, C, D) are the direct result of 1:2 or 1:4 additions to the conjugated systems in the quinone. Two others (B and E) are secondary products derived from direct addition products, while F is the only product whose formation could not have been predicted from a consideration of the addition reactions of conjugated systems

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[3] (a) Haller and Guyot, *Bull. soc. chim.*, **31**, 795 (1904); (b) Guyot and Staehling, *ibid.*, **33**, 1104, 1144 (1905); (c) Clarke and Carleton, THIS JOURNAL, **33**, 1966 (1911); (d) Werner and Grob, *Ber.*, **37**, 2887 (1904); (e) Bischoff, *Ber.*, **38**, 2078 (1905); (f) Bamberger and Blangey, *Ber.*, **36**, 1625 (1903); (g) *Ann.*, **384**, 272 (1911); (h) Franssen, *Bull. soc. chim.*, **37**, 902 (1925).

alone. But the combined amount of these six products accounted for only one-fourth of the reagents used. Another fourth of the quinone was reduced to hydroquinone and the rest of the material turned up as amorphous material, tars and oils. Thus the reactions leading to the formation of these solid products were not the only ones taking place and there must have been several more occurring which were impossible to study. These results of Bamberger and Blangey are typical of all the published work in this field dealing with quinones in which the conjugated systems are open to attack by a Grignard reagent. In every such case the reaction gives more tars, oils and amorphous materials than anything else.

In the present work we have found that duroquinone, though a completely substituted quinone, gives the same sort of results that Bamberger and Blangey found xyloquinone produced. The yield of solid addition products is extremely low and by far the greater amount of the material turns up as an uncrystallizable oil, although we obtained no tars or amorphous material.

## Choice of Grignard Reagent

Preliminary experiments with the reaction between duroquinone and Grignard reagents showed that large amounts of a yellow oil are produced. In order to determine whether or not the nature of the Grignard reagent was a factor in the production of this oil, we added the following to the quinone: methylmagnesium iodide, methylmagnesium bromide, ethylmagnesium bromide, phenylmagnesium bromide and $\alpha$-naphthylmagnesium bromide. In every case large amounts of oil were formed and the amount of this oil is practically independent of the nature of the Grignard reagent. Because of this, our first detailed experiments were carried out using ethylmagnesium bromide, as this particular reagent was the easiest one for us to prepare in quantity.

Our next experiments were undertaken to determine quantitatively the amount of ethylmagnesium bromide which would react with a given quantity of duroquinone. Using a standard solution of the reagent and the procedure and apparatus of Gilman,[4] it was found that 1.6 moles of ethylmagnesium bromide react per mole of quinone but that a considerable amount of gaseous by-product results. This gas was collected and analyzed but the results of the analysis do not correspond with the calculated values for methane, ethane, ethylene or butane. About 10% of the gas is unsaturated (absorbed by concd. sulfuric acid or bromine water), and the remainder is a mixture of saturated hydrocarbons. We have assumed that this gas results from reactions of the Wurtz type and, since it is a rather complicated mixture and difficult to study, ethylmagnesium

[4] Gilman and Crawford, This Journal, **45**, 554 (1923).

bromide was discarded and phenylmagnesium bromide substituted for it. If the reactions producing the gaseous by-products are actually of the Wurtz type, then with phenylmagnesium bromide diphenyl and compounds related to it should result. These compounds are solids and the use of phenylmagnesium bromide in place of ethylmagnesium bromide should, if the two reagents behave in the same way, lead to by-products which would be easier to handle than the mixture of gases resulting when ethylmagnesium bromide is used. Our preliminary experiments justified these expectations; no gases are evolved when phenylmagnesium bromide is added to duroquinone and, therefore, we chose this particular Grignard reagent for the rest of our work.

## Discussion of the Reaction

When duroquinone reacts with phenylmagnesium bromide, the yield and nature of the products, as well as the color changes taking place during the reaction, vary with the procedure and with the relative amounts of the two reagents used. When the Grignard reagent is added to the quinone, the color changes from yellow to orange to green as the metallic addition product is formed. When the reagents are added in the reverse order, the color becomes green at first, and then the solid addition product dissolves in the excess Grignard reagent, giving a yellow solution. Later, a heavy, yellow oil separates out below the ether layer. In either case the primary reaction product is a mixture of metallic derivatives which may be decomposed either by acids or by acetyl chloride. If acids are used for the decomposition, there results a mixture of hydroxyl compounds, practically all of which are "enols" and may rearrange partly or entirely into the corresponding keto forms. If acetyl chloride is used for the decomposition, the acetates of these hydroxyl compounds result. These acetates are stable and do not rearrange and, as they can be hydrolyzed later to give the hydroxyl compounds, the isolation, separation and purification of the reaction products is often greatly facilitated by using acetyl chloride instead of hydrochloric acid for the decomposition. The use of acetyl chloride for this purpose has the further great advantage of giving fewer compounds, for a pair of keto-enol isomers corresponds to only one metallic derivative and, consequently, to only one acetate. It is very interesting in this connection that benzoyl chloride and dimethyl sulfate are without effect upon these metallic derivatives—no benzoates or methyl ethers result and the magnesium derivatives remain unchanged after several hours' boiling with either of these reagents.

After decomposition of the metallic derivatives by hydrochloric acid or acetyl chloride the ether layer was separated, the aqueous layer extracted two or three times with ether and all the ether solutions were combined and evaporated to crystallization. After the solids were filtered off and the ether was fully evaporated from the mother liquor, there remained a dark, thick oil. This oil constitutes about 80% of the reaction product, the other 20% appearing as solid products. No amorphous substances were obtained and the amount of tarry material was very small.

Aside from hydroduroquinone and diphenyl, which are always formed, the solid addition products can be divided into two classes, as follows.

1. Mono-addition products, or their acetates, formed in accordance with the following equations (written as though $C_6H_6$ were added):

$$C_{10}H_{12}O_2 + C_6H_6 \longrightarrow C_{16}H_{18}O_2, \text{ or}$$
$$C_{10}H_{12}O_2 + C_6H_6 + CH_3COCl \longrightarrow C_{18}H_{20}O_3 + HCl$$

2. Di-addition products, or their di-acetates, formed in accordance with the following equations

$$C_{10}H_{12}O_2 + 2C_6H_6 \longrightarrow C_{22}H_{24}O_2, \text{ or}$$
$$C_{10}H_{12}O_2 + 2C_6H_6 + 2CH_3COCl \longrightarrow C_{26}H_{28}O_4 + 2HCl$$

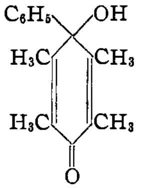
In general, when an excess of duroquinone is used, the mono-addition compounds are the chief products, while an excess of the Grignard reagent leads chiefly to the di-addition products. As mentioned above, the solid products constitute only 20% of the reaction mixture, the other 80% appearing as an oil. Since we were interested particularly in the solids, some preliminary experiments were conducted, varying the procedure and relative amounts of reagents in order to determine the best conditions for the production of solid material. In each experiment 10 g. of quinone was used and the result may be summed up briefly as follows. The largest amount of solid obtained in one run was 1.8 g. and the amount varied from this down to a mere trace. The largest amount of oil produced was 19.8 g. and in this case it was not accompanied by any solid material at all. The amount of quinone reacting varied from 0.9 to 10 g., that is, the amount of quinone recovered unchanged varied from 9.1 g. to zero. As a result of these experiments, we chose the following two procedures as giving the largest amounts of solid reaction products and the rest of our experiments were carried out according to one or the other of these procedures. Method (1): one equivalent of phenylmagnesium bromide was added to one equivalent of duroquinone, followed by decomposition of the metallic addition product by dilute hydrochloric acid. In this method the quinone is in excess until the end of the reaction and the solid products are chiefly mono-addition compounds. Method (2): one equivalent of duroquinone was added to four equivalents of phenylmagnesium bromide, followed by decomposition of the metallic addition products by acetyl chloride. In this method the Grignard reagent is in excess and the solid products are chiefly the di-addition compounds. In all our experiments we found the yields to be extremely variable, and two experiments, apparently conducted exactly alike, often gave different results. Because of this we always carried out our reactions with small amounts (10 to 20 g.) of duroquinone.

## Discussion of the Reaction Products

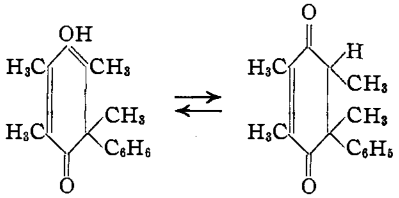
**A. Compounds Formed by the Addition of One Molecule of Phenylmagnesium Bromide to One Molecule of Duroquinone.**—When the reaction is carried out according to Method (1), the chief solid products are a yellow substance, m. p. 142°, and two white substances, m. p. 150 and 203°, all of which have the composition and molecular weight represented by the formula $C_{16}H_{18}O_2$. This composition corresponds to the addition of $C_6H_6$ to duroquinone

$$C_{10}H_{12}O_2 + C_6H_6 \longrightarrow C_{16}H_{18}O_2$$

It is possible to write three structural formulas corresponding to this composition which could result from the addition of one molecule of phenylmagnesium bromide to duroquinone, followed by hydrolysis. One of these (I) represents a 1:2 addition product and the other two represent the 1:4 addition product (IIA) and its keto form (IIB)



I (203°)



IIA (150°) IIB (142°)

The yellow compound, m. p. 142°, on oxidation with potassium permanganate in acetone gives acetophenone as one of the products. Since methyl and phenyl groups are attached to the same carbon atom in acetophenone, they must have been attached to the same carbon atom in the 142° compound, which eliminates structure I for this compound. When the 142° compound is ozonized, or oxidized very carefully by potassium permanganate, one of the products is a white acid having the composition $C_{12}H_{14}O_4$. If a substance with the structure represented by IIB were ozonized, one of the decomposition products to be expected would be $\alpha,\beta$-dimethyl-$\alpha$-phenyl succinic acid, $CH_3CH(COOH)C(CH_3)(C_6H_5)COOH$, $C_{12}H_{14}O_4$. A substance having the structure IIA, when ozonized, could not give any dibasic acid having the composition $C_{12}H_{14}O_4$, but would give the keto acid $CH_3COC(C_6H_5)(CH_3)COOH$, or its decomposition products, $CH_3COCH(CH_3)C_6H_5$ and $C_6H_5CH(CH_3)COOH$, none of which have the composition $C_{12}H_{14}O_4$. Structure IIB, then, correctly represents the yellow compound melting at 142°.

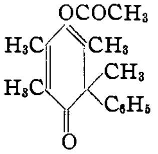
Both the 142° compound, (IIB), which is yellow, and the 150° compound, which is colorless, melt without decomposition to give yellow liquids. On cooling, these two substances solidify again, but when remelted the melting points show a drop until, after the fifth or sixth remelting, the two substances show approximately the same melting point (110°) and no longer solidify on cooling. This final melting point is practically the same as the melting point of a 1–1 mixture of the 142 and 150° compounds. The 203° compound shows no change in melting point after repeated melting and solidifying. This behavior indicates that the 142 and 150° compounds are the pair of keto-enol isomers IIA and IIB.

The 150° compound acetylates readily, giving a mono-acetate melting at 140°, and methylates easily to give a monomethyl derivative melting at 115°. All attempts to acetylate or methylate the 142° compound resulted in a yellow oil and unchanged material.

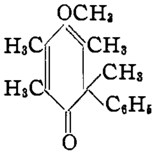
That the 150 and 142° mono-addition products as well as the 140° mono-acetate are closely related is shown by the following experiment, in which these three substances were all obtained from the same metallic derivative.

A reaction product obtained by adding one equivalent of phenylmagnesium bromide to 20 g. of duroquinone was divided into two parts. One part was decomposed with dilute hydrochloric acid and gave 0.45 g. of the 150° compound and 0.65 g. of the 142° compound. The other part was decomposed with acetyl chloride and gave 1.8 g. of the 140° mono-acetate. The amount of mono-acetate obtained corresponds to somewhat more than the combined amounts of the 150 and 142° compounds, but this may be accounted for by the fact that the acetates of these compounds are always more easily isolated from reaction mixtures than the unacetylated compounds. As is often the case, the 203° compound was not formed in this experiment. It never results in large amounts and the yield of it varies from zero to 2 g. per 50 g. of quinone.

These results indicate that the 150 and 142° mono-addition products are a pair of keto-enol isomers, and since the 142° compound has the structure IIB, the 150° compound must have the structure IIA. This leaves the structure I for the 203° mono-addition product, while the 140° mono-acetate has the structure III and the 115° methyl ether the structure IV



III



IV

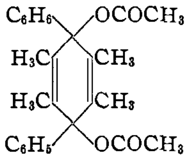
In several experiments according to method (1) there resulted small amounts of a red solid melting at 95°. This substance, in alcohol, gives a yellow solution of about the same intensity as duroquinone and on attempting to recrystallize it duroquinone was always found in the product. When steam distilled this red substance gives a distillate containing duroquinone and leaves a residue of the white compound, IIA. When equivalent amounts of the 150° compound, IIA, and duroquinone are dissolved in alcohol, the solution deposits red crystals, m. p. 95°, identical with those obtained from the original reaction mixture. This 95° compound is therefore a molecular compound of duroquinone and the 150° compound, IIA.

In one experiment according to method (1) a small amount of an orange compound, m. p. 135°, was obtained. This substance gives duroquinone on steam distillation but the residue is an oil. It has the same composition as the 95° molecular compound and is evidently another molecular compound of duroquinone and one of the mono-addition products, although we did not succeed in synthesizing it.

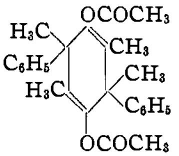
Method (1) also occasionally gives some dark green needles of the quinhydrone of duroquinone. It can be obtained by crystallizing a mixture of duroquinone and hydroduroquinone.

**B. Compounds Formed by the Addition of Two Molecules of Phenylmagnesium Bromide to One Molecule of Duroquinone.**—The chief solid products of reactions carried out according to method (2) are the 140° mono-acetate III, the diacetate of hydroduroquinone and a white compound melting at 245° and having the composition $C_{26}H_{28}O_4$. This composition corresponds to the addition of 2 molecules of $C_6H_6$ to one of duroquinone, followed by a double acetylation of the product, and its reactions show that the compound is a diacetate.

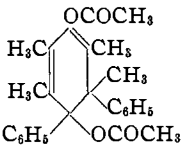
It is possible to write three structures which represent diacetates that could result from the addition of two molecules of phenylmagnesium bromide to one of duroquinone, followed by decomposition with acetyl chloride. These are V, in which both additions are 1:2 to carbonyl; VI in which both are 1:4 to the conjugated systems; and VII in which one addition is 1:2 and one 1:4.



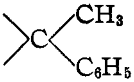
V



VI (245°)

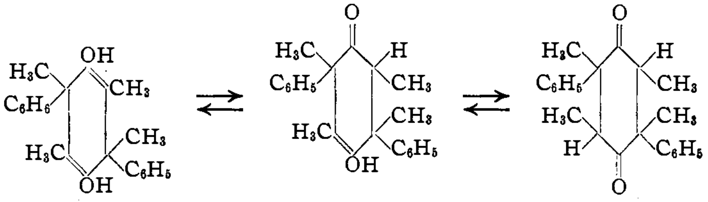


VII

The 142° mono-addition compound, IIB, reacts with phenylmagnesium bromide to give a metallic derivative which, when decomposed with acetyl chloride, gives the 245° diacetate and a dark oil. This eliminates structure V for that of the 245° diacetate, for the compound IIB has been shown to contain the grouping  $>C<^{CH_3}_{C_6H_5}$ which does not occur in V. Structure VII for this diacetate is eliminated as follows. A compound of this structure could result by acetylating either the product of 1:4

addition of phenylmagnesium bromide to I, or the product of a 1:2 addition of phenylmagnesium bromide to IIA or IIB; while VI cannot be obtained from the mono-addition products in any other way than by a 1:4 addition to IIA or IIB. The 203° compound, I, reacts with phenylmagnesium bromide, but the product on decomposition with either hydrochloric acid or acetyl chloride is a yellow oil and none of the very sparingly soluble 245° diacetate can be isolated from it. This leaves structure VI for the 245° diacetate.

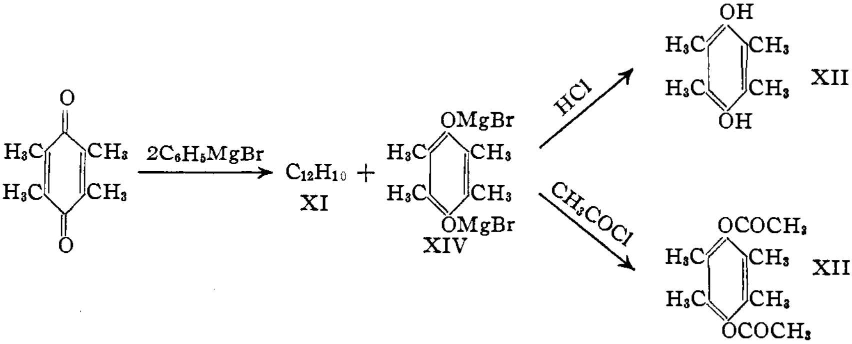
When this diacetate is hydrolyzed, the products are solids which melt anywhere from 110 to 197°. None of the products of a fractional crystallization of these solids shows a constant melting point but all the fractions, no matter what the melting-point, give the same analyses and acetylate easily to give the 245° diacetate again. The composition of these solids is $C_{22}H_{24}O_2$, corresponding to the addition of $2C_6H_6$ to duroquinone. If the diacetate, VI, is hydrolyzed, the first product should be dihydroxyl compound VIII, which could isomerize to the two tautomeric forms IX and X.



VIII IX X

The variable melting point of the solids obtained by hydrolyzing the diacetate is due to the establishment of equilibria between these three tautomers. All of them have the same composition and all three would, on acetylation, give the same diacetate.

**C. By-products which Result, Regardless of Procedure.**—Diphenyl, XI, and hydroduroquinone XII (or its diacetate, XIII, if the metallic derivatives are decomposed with acetyl chloride), are formed in small amounts in all reactions between the quinone and phenylmagnesium bromide and result from the reducing action of the Grignard reagent.



The three compounds XI, XII and XIII were all identified by comparison with known samples.

The thick, viscous oils, accounting for 75 to 80% of the reaction product, were obtained in all the reactions between the quinone and Grignard reagents, regardless of whether the metallic derivatives were decomposed with hydrochloric acid or acetyl chloride. This oil usually contains about 20% of quinone (and hydroquinone or its diacetate), which may be removed by adding $FeCl_3$-HCl to oxidize any hydroquinone and then distilling with steam, as the oil is only slowly volatile with steam. The residue from the steam distillation is a red oil only a small part of which (less than 10%) is alkali soluble. It cannot be distilled without considerable decomposition, even under reduced pressure, and shows no constant boiling point—thus, a sample of 34 g. gave 21 g. of distillate, b. p. 200–250° under 26 mm., and 10 g. of dark, tarry residue. We were not able to obtain any solid derivatives of this oil; it apparently does not react with dimethyl sulfate or acetyl chloride—at least the products are oils. It reduces potassium permanganate but the product is an oil which is not soluble in alkali and which gives only oils with phenylhydrazine. Bromination gives hydrobromic acid and a thick, red oil. Boiled with concd. nitric acid, it gives a yellowish semi-solid which gives only oils when attempts are made to recrystallize it.

No conclusions can be drawn regarding the nature of this oil other than to call attention to the fact that almost all of the solid products obtained in the reaction contain one or more asymmetric carbon atoms, and the oil may be a mixture of stereoisomers, as suggested by Kohler and Butler[5] in the case of oils which they obtained in some analogous reactions with the Grignard reagents and unsaturated carbonyl compounds.

## Experimental Part[6]

### Preparation and Purification of Reagents

**Bromobenzene.**—This was prepared by brominating benzene in the usual way. The product was fractionated twice, using a Glinsky column, and the fraction boiling at 150–154° under 738 mm. was considered pure enough for the purpose.

**Magnesium.**—This was a pure specimen, leaving almost no residue after reacting with bromobenzene.

**Ether.**—This was purified by shaking with water to remove alcohol and then with potassium permanganate. After standing over calcium chloride for a week, and then over phosphorus pentoxide for a day, it was distilled directly from the phosphorus pentoxide and kept over sodium wire.

**Duroquinone.**—This was made by the method described by Smith and Dobrovolny.[7]

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[5] Kohler and Butler, THIS JOURNAL, **48**, 1047 (1926).

[6] The carbon-hydrogen analyses were carried out by the semi-micro method developed in this Laboratory by W. M. Lauer.

[7] Smith and Dobrovolny, THIS JOURNAL, **48**, 1420 (1926).

## Details of Procedure

**Method (1).**—One-tenth of a mole of phenylmagnesium bromide in ether was added, through a dropping funnel, to an ether solution of 10 g. of duroquinone (0.061 mole) in a liter round-bottomed flask fitted with a reflux condenser and a calcium chloride guard tube. The flask was shaken frequently during the addition and the metallic addition product deposited as a bright yellowish green solid. The reaction mixture, after standing overnight, was decomposed with iced hydrochloric acid. The layers were separated, the water layer was extracted several times with ether, all the ether solutions were combined, dried over calcium chloride and then evaporated to about 40 cc. Solid material was deposited on cooling. This was filtered off and recrystallized. It was the 142° mono-addition compound, IIB. Five runs, each of 10 g. of duroquinone, gave 1.6, 2.7, 2.1, 2.0 and 3.4 g., an average of 2.3 g. per 10 g. of quinone. The oily residues from these runs were combined and, after standing for several days, it deposited a small amount of the 203° compound I. Later, a small amount of the 95° red molecular compound crystallized out and there remained 73 g. of oil which, on steam distillation, gave some duroquinone and diphenyl. The 203° compound I was usually mixed with the 142° compound IIB, and since their solubilities are so nearly the same, the only means of separation was to pick out the two different kinds of crystals (white and yellow) with a small pair of tweezers under a large lens; yield from 50 g. of duroquinone: 11.8 g. of 142° compound IIB, 2.0 g. of 203° compound I, small amount of 95° molecular compound, 73 g. of oil. It is not possible, however, to give much more than a general idea as to yields of the various products for the yields vary widely, even when apparently identical procedures are used.

**Method (2).**—Phenylmagnesium bromide was prepared from 38.3 g. of bromobenzene and 5.85 g. of magnesium. After the reaction was completed, the ethereal solution of phenylmagnesium bromide was poured into a dry, liter round-bottomed flask fitted with reflux condenser and dropping funnel. A solution of 10 g. of duroquinone in ether was slowly added from the dropping funnel, with frequent shaking. The reaction product was a green solid which dissolved in the excess of phenylmagnesium bromide to give a yellow solution. After about three-fourths of the quinone had been added, a heavy yellow oil settled out below the ether. When the quinone was all added, the reaction mixture was allowed to stand for several hours and was then decomposed by adding 21 g. of acetyl chloride through the dropping funnel. This amount of acetyl chloride is a slight excess calculated on the phenylmagnesium bromide used. The solution was heated on the steam-bath for half an hour and then water was added to decompose the excess acetyl chloride. The layers were separated, the water layer was extracted several times with ether and all the ether solutions were combined. Any solid material (the diacetate VI) suspended in the ether was filtered off, the filtrate dried over calcium chloride and evaporated to about 75 cc. The diacetate VI crystallized on cooling. This was filtered off and the filtrate allowed to concentrate by evaporation, when the diacetate of hydroduroquinone, m. p. 202° (XIII), appeared. On longer standing the filtrate deposited the 140° mono-acetate (III) and a dark viscous oil remained; yield from 10 g. of quinone, 2.35 g. of 245° diacetate (VI), 1.3 g. of 202° diacetate of hydroduroquinone (XIII), 0.75 g. of 140° monoacetate (III) and 23 g. of oil. If the reaction product is steam distilled immediately after the decomposition with acetyl chloride diphenyl may be isolated from the distillate. The residue from the steam distillation is then extracted with ether and the separation of solids carried out as before.

## Properties and Reactions of the Individual Solid Products

**2,3,5,6 - Tetramethyl - 1 - phenylcyclohexadiene - 2,5 - one - 4 - ol - 1** (I) crystallizes from alcohol or ether in hard, colorless, transparent prisms, m. p. 203°. It does not form a semicarbazone or phenylhydrazone, gives a yellow oil on acetylation and is recovered unchanged on treatment with dimethyl sulfate. Oxidation with potassium permanganate gives a yellow oil which is not soluble in sodium bicarbonate. It reacts with phenylmagnesium bromide to give a metallic derivative, but on acidification an oil results, along with diphenyl.

*Anal.* Calcd. for $C_{16}H_{18}O_2$ (242): C, 79.3, H, 7.5. Found: C, 79.2, 79.6, 79.4, 79.1; H, 7.4, 7.3, 7.7, 7.6.

*Mol. wt.* Subs., 0.1506, 0.1506; benzene, 13.88, 19.97. $\Delta T$, 0.185°, 0.132°; mol. wt., 293, 285.

**2,3,5,6-Tetramethyl-3-phenylcyclohexadiene-1,5-one-4-ol-1** (IIA) crystallizes from alcohol in colorless, square, transparent plates, m. p. 150°. It does not react with phenylmagnesium bromide. Oxidation with potassium permanganate gives an oil partly soluble in sodium carbonate. It acetylates easily and methylates with dimethyl sulfate and alkali. It forms a red molecular compound with duroquinone.

*Anal.* Calcd. for $C_{16}H_{18}O_2$ (242): C, 79.3, H, 7.5. Found: C, 79.5, 78.9, 79.2; H, 7.4, 7.4, 7.4.

*Mol. wt.* Subs., 0.0857, 0.0857; benzene, 15.385, 27.73. $\Delta T$, 0.105°, 0.063°; mol. wt., 264, 245.

**Derivatives.**—Acetate (III), white needles, m. p. 140°, extremely soluble in alcohol and ether. Does not decolorize potassium permanganate on standing for 24 hours. Does not react with phenylmagnesium bromide. Requires alcoholic potash or sodium ethylate for hydrolysis, and the product is the parent compound, IIA.

*Anal.* Calcd. for $C_{18}H_{20}O_3$ (284): C, 76.0, H, 7.1; Found: C, 76.0, 75.8, 75.9; H, 7.1, 7.1, 7.2.

*Mol. wt.* Subs., 0.3000, 0.3000; bromoform, 40.024, 65.58. $\Delta T$, 0.380°, 0.233°; mol. wt., 284, 283.

METHYL ETHER (IV) crystallizes in long, white needles from methyl alcohol; m. p. 115°. Is not oxidized by potassium permanganate.

*Anal.* Calcd. for $C_{17}H_{20}O_2$ (256): C, 79.6, H, 7.9. Found: C, 79.4, H, 8.7.

MOLECULAR COMPOUND WITH DUROQUINONE.—Crystallizes from alcohol, in which it is quite soluble, in bright red prisms, m. p. 95°. The alcoholic solution has the pale yellow color of duroquinone.

*Anal.* Calcd. for $C_{10}H_{12}O_2 + C_{16}H_{18}O_2 = C_{26}H_{30}O_4$: C, 76.8, H 7.4. Found: C, 76.5, 77.7; H, 7.2, 7.4.

*Mol. wt.* Subs., 0.1511, 0.1511; benzene, 15.07, 20.57. $\Delta T$, 0.258°, 0.181°; mol. wt., 194, 203. Calcd. for $^1/_2$ ($C_{10}H_{12}O_2 + C_{16}H_{18}O_2$), 203.

**2,3,5,6-Tetramethyl-3-phenylcyclohexene-5-dione-1,4** (IIB) is quite soluble in alcohol and ether, from which it crystallizes in hard, transparent, yellow hexagons, m. p., 142°. It reacts with phenylmagnesium bromide to give a metallic derivative which, decomposed with acetyl chloride, gives the 245° diacetate VI. Does not react with phenylhydrazine or hydroxylamine, and with semicarbazide gives an isomeric compound, m. p. 62°, which contains no nitrogen. Acetylation gives a yellow oil and unchanged material. Methylation with dimethyl sulfate and alkali gives an oil and unchanged material, but attempted methylation with methyl iodide and sodium methylate gives the same isomeric compound, m. p. 62°, that is obtained when attempts are made to form a semicarbazone. Bromination gives a yellow oil.

*Anal.* Calcd. for $C_{16}H_{18}O_2$ (242): C, 79.3, H, 7.5. Found: C, 79.4, 78.8; H, 7.4, 7.4.

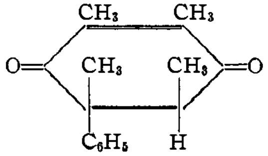
*Mol. wt.* Subs., 0.1506, 0.1500; benzene, 14.21, 13.25. $\Delta T$, 0.224°, 0.232°; mol. wt., 237, 244.

Oxidation.—One g. of the solid was dissolved in 50 cc. of acetone, the solution cooled and powdered potassium permanganate added as long as any decolorization took place (about 1.7 g. of potassium permanganate). The solution became brown at once but no manganese dioxide precipitated until about 1 g. of potassium permanganate had been added. The solution was then warmed to room temperature, when a little more potassium permanganate reacted, after which it was poured onto iced sulfuric acid and decolorized with sodium bisulfite. The solution was extracted with ether and the aqueous layer discarded. The ether layer was extracted with sodium bicarbonate. and the bicarbonate solution, on acidification, gave a precipitate of a white acid; m. p. 170–172°. The ether layer was evaporated and the residue (oil), when treated with semicarbazide, gave the semicarbazone of acetophenone. Ozonization in carbon tetrachloride gives a viscous oil from which the same acid, m. p. 170–172°, can be extracted with sodium bicarbonate, but no acetophenone results. This acid is slightly soluble in cold water but dissolves in boiling water, from which it crystallizes slowly on cooling. It is difficultly soluble in benzene but very soluble in ether.

*Anal.* Calcd. for $C_{12}H_{14}O_4$: C, 64.9; H, 6.4. Found: C, 65.6, 65.2; H, 6.6, 6.8.

*Eq. wt.* Subs., 0.1568; NaOH (0.1188 *N*) 11.8 cc. = 0.0560 g. of NaOH. Eq. wt., 112. The simplest formula which will satisfy both the analysis and equiv. wt. determination and which contains a phenyl group is $C_{12}H_{14}O_4$, mol. wt. 224, and from its method of formation, and the fact that acetophenone usually accompanies it, we regard this acid as $\alpha,\beta$-dimethyl-$\alpha$-phenyl succinic acid, $CH_3CH(COOH)C(CH_3)(COOH)C_6H_5$. Several attempts were made to synthesize this substance, but none of them was successful.

As mentioned above, when the compound IIB is treated with semicarbazide, or with methyl iodide and alkali, it gives a pale yellow, isomeric substance; m. p. 62°. So little of this material was available that no extensive investigation of it could be made. When fused and inoculated with a crystal of the 142° compound IIB, the substance undergoes no change. We are inclined to regard it as a geometric isomer of the 142° compound, which is the only mono-addition compound capable of existing in two geometric forms.



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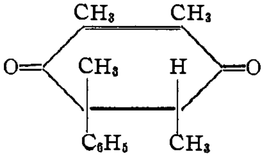

*Anal.* Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5. Found: C, 78.4, 79.7; H, 7.9, 7.8.

**Molecular compound,** $C_{16}H_{18}O_2$ + duroquinone.—About 0.2 g. of an orange compound, m. p., 135°, was obtained once in a reaction carried out according to method (1). It is soluble in alcohol, from which it crystallizes in orange plates. On standing this orange compound turns yellow. Distillation with steam gives duroquinone and leaves a residue of oil which apparently contains no solid material.

*Anal.* Calcd. for $C_{16}H_{18}O_2 + C_{10}H_{12}O_2$: C, 76.8; H, 7.4. Found: C, 76.7, 77.3; H, 7.5, 7.6.

The compound is apparently a molecular compound of duroquinone and one of the mono-addition products, but we were not able to synthesize it by crystallizing together duroquinone and any of the mono-addition products.

**Di-addition Compounds,** $C_{22}H_{24}O_2$ **(VIII, IX** or **X).**—The di-addition product is best obtained by isolating it from the reaction product as the diacetate and then hydrolyzing. It is a white solid, very soluble in alcohol or ether, from which it recrystallizes in fairly large needles. The melting point varies with the procedure and recrystallization of the various fractions does not lead to any definite separation. The melting points of the products we obtained varied from 115 to 197°. All of these products gave the same analyses and acetylated easily to give the same diacetate. The substance is very stable—it does not reduce potassium permanganate, and it merely acetylates when boiled with chromic acid in glacial acetic acid. It does not react with semicarbazide. All attempts to methylate it, using dimethyl sulfate and alkali, gave unchanged starting material. It reacts with bromine in carbon tetrachloride to give hydrobromic acid and a white, monobromo compound; m. p. 163–164°. *Anal.* Calcd. for $C_{22}H_{23}O_2Br$: Br, 20.0. Found: Br, 20.9.

*Anal.* Calcd. for $C_{22}H_{24}O_2$: C, 82.5; H, 7.6. Found (a) sample, m. p. 184°, direct from Grignard reaction: C, 81.1, 81.6; H, 7.3, 7.4; (b) sample, m. p. 144°, from hydrolysis of the diacetate: C, 82.2, 81.7; H, 7.8, 7.3; (c) sample, m. p. 197°, from hydrolysis of the diacetate: C, 82.1, 81.9; H, 7.2, 7.6; (d) sample, m. p. 115°, from hydrolysis of the diacetate: C, 79.8, 81.4; H, 7.5, 7.8.

*Mol. wt.* Subs., 0.1505, 0.1505; benzene, 14.94, 20.27. $\Delta T$, 0.163°, 0.121°; mol. wt., 308, 307. Calcd. for $C_{22}H_{24}O_2$, 320.

The substance acetylates easily and quantitatively when its solution in acetic anhydride is treated with a drop of concd. sulfuric acid and warmed for an hour. Because of this easy acetylation we have written the structure chiefly as the diol VIII, but the melting points of the different samples indicate that it is a mixture.

**2,3,5,6-Tetramethyl-3,6-diphenylcyclohexadiene-1,4-diol-1,4-diacetate** (VI).—This substance is obtained by acetylating any of the di-addition products, or it may be obtained directly from the product of the Grignard reaction according to method (2) by decomposing the metallic derivatives with acetyl chloride. It is only slightly soluble in alcohol, ether and benzene but quite soluble in chloroform, bromoform and carbon tetrachloride. It crystallizes from a mixture of chloroform and ethyl alcohol in small, white prisms; m. p. 245°. It is extremely stable and is not affected by potassium permanganate, chromic acid or ozone. It can be hydrolyzed by 60% sulfuric acid, but better results are obtained if it is refluxed with sodium ethylate. Five g. refluxed with a solution of 2 g. of sodium in 100 cc. of 95% ethyl alcohol for ten hours, followed by standing overnight, gave 2.04 g. of solid, m. p. 165°, and the filtrate diluted with water, acidified and then extracted with ether gave, as the ether evaporated, the following solids: 0.289 g., m. p. 155°; 0.025 g., m. p. 140°; 0.659 g., m. p. 133°; 0.228 g., m. p. 115°; 0.040 g., m. p. 110–117° and a small amount of yellow oil. Total solids, 3.28 g. Theory from 5 g. of diacetate, 3.96 g. All of these solids acetylated easily to give the same diacetate.

*Anal.* Calcd. for $C_{26}H_{28}O_4$: C, 77.2, H, 7.0. Found: C, 76.4, 76.6, 76.4; H, 6.9, 6.9, 6.8.

*Mol. wt.* Subs., 0.3000, 0.2000, 0.2000; bromoform, 62.33, 56.01, 84.83. $\Delta T$, 0.180°, 0.133°, 0.087°; mol. wt., 385, 387, 390. Calcd. for $C_{26}H_{28}O_4$: 404.

All the other solid products obtained were known and were identified by their mixed melting points with prepared specimens. These compounds were: diphenyl, m. p. 69°; hydroduroquinone, m. p. 230°; and hydroduroquinone diacetate, m. p. 202°. One new derivative of hydroduroquinone was made in the course of the work, namely, the dibenzoate. Two equivalents of phenylmagnesium bromide was added to one equivalent of hydroduroquinone suspended in ether. A bright robin's egg blue color developed. After the reaction was complete, an excess of benzoyl chloride was added. The solution became yellow and a white solid settled out. Recrystallized from a mixture of chloroform and ethyl alcohol, it melted at 259–260°. It was very difficult to burn completely in the combustion apparatus.

*Anal.* Calcd. for $C_{24}H_{22}O_4$: C, 77.0; H, 5.9. Found: C, 76.9, 76.5; H, 6.7, 6.3.

No oily by-products were obtained in this reaction, and none result when the diacetate of hydroduroquinone is made in the same way. Hence the oils obtained when the quinone reacts with the Grignard reagent are not formed from the hydroquinone. But the blue color which develops when phenylmagnesium bromide is added to hydroduroquinone may, with the yellow of the quinone, be the cause of the green color which always appears as the reaction between duroquinone and phenylmagnesium bromide takes place.

## Summary and Conclusions

1. Several Grignard reagents have been added to duroquinone.
2. With phenylmagnesium bromide, twelve solids were isolated from the reaction mixture. Four of these were already known and the other eight have been described in this paper, together with three other new compounds which were not obtained directly from the reaction mixture.
3. In so far as a quinone is comparable to an $\alpha$-$\beta$ unsaturated ketone, the solid products of the reaction are those which would be expected.
4. Compounds were formed by a reaction involving the 1:6 system in the quinone, but two molecules of Grignard reagent were necessary and this reaction cannot be considered a 1:6 addition in the usual sense.
5. There is no evident relationship between the results of this work and those obtained by Smith and Dobrovolny on the addition of sodium malonic esters to duroquinone. This lack of relationship between the two pieces of work supports the interpretation already given for the malonic ester reaction: namely, that it is an oxidation in the presence of alkali, which could not occur in the work with the Grignard reagent.
6. About 80% of the reaction product between duroquinone and any Grignard reagent is an oil which may be a mixture of stereoisomers This oil cannot be crystallized nor can it be distilled undecomposed.

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