[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

# The Reactions of Phenanthrenequinone and 2,5-Di-*t*-butyl-1,4-benzoquinone with Phenyllithium and with Phenylmagnesium Bromide[1,2]

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RECEIVED FEBRUARY 26, 1952

Phenanthrenequinone reacts with phenyllithium to give only the known *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydrophenanthrene. 2,5-Di-*t*-butyl-1,4-benzoquinone reacts with phenyllithium and with phenylmagnesium bromide to give only one product, that resulting from the addition of two molecules of the organometallic reagent to the carbonyl groups The resulting diol loses water and rearranges to give a phenol. The acetate of this phenol and the diacetate of 2,5-di-*t*-butylhydroquinone have been prepared.

In general, the reactions between quinones and Grignard reagents do not give good yields. In view of the excellent yields (92–98%) obtained when anthraquinone[3] and 2,3-diphenyl-1,4-naphthoquinone[4] were treated with phenyllithium, it seemed desirable to extend the study of the use of phenyllithium to other quinones.

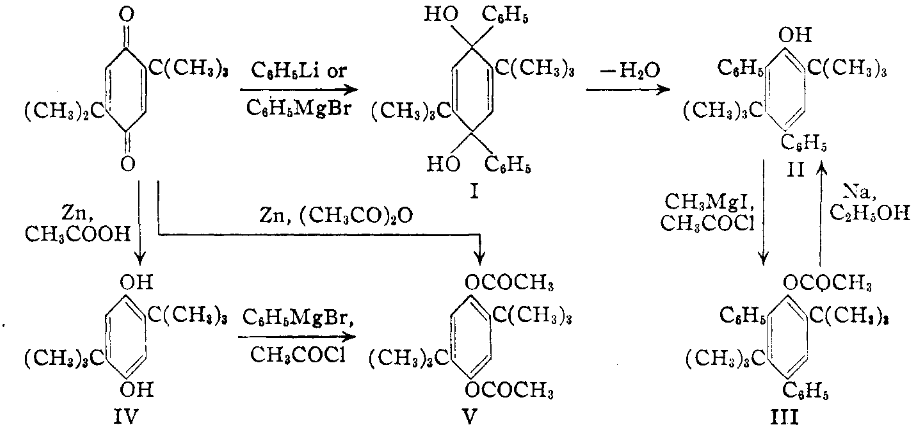
In the case of phenanthrenequinone, the known *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydrophenanthrene (melting at 180–181°) was formed in yields varying from 0.5–22%. Bachmann[5] and Acree[6] obtained this same diol in 70–74% yields, using phenylmagnesium bromide.

Variations in the conditions under which the reaction was carried out seemed to make little difference in the yield of the diol. In general, large excesses of phenyllithium and heating decreased the yields. The best yields (14–22%) were obtained by adding a suspension of 0.05 mole of the quinone in dry benzene to an ether solution containing approximately 0.2 mole of phenyllithium.

After recrystallizing most of the diol a small amount of a compound melting at 183–184° was obtained. It was recovered unchanged after procedures which would be expected to hydrolyze ethers or acetals and its structure has not been determined.

Some reduction to the hydroquinone always occurred when either phenyllithium or phenylmagnesium bromide reacted with 2,5-di-*t*-butyl-1,4-benzoquinone, and biphenyl could always be detected. In some reactions with phenylmagnesium bromide the yield of the hydroquinone (IV) was around 50%. Oesper, Smyth and Kharasch[7] prepared this hydroquinone from *t*-butyl alcohol and hydroquinone. Reduction of the quinone by zinc dust and 80% acetic acid gave the hydroquinone in 95–98% yields. The diacetate of this hydroquinone (V) was prepared from the hydroquinone and by reductive acetylation of the quinone.

Despite variations in amounts of reactants and in the method of carrying out the reaction, no monoaddition product and no 1,4-addition product could ever be isolated. The same diaddition product (I) was formed whether phenyllithium or phenylmagnesium bromide was used, and was the compound resulting from the addition of two molecules of the organometallic reagent to the carbonyl groups of the quinone. The yields with phenyllithium varied from 35 to 60% while phenylmagnesium bromide gave only 5 to 10% of I. Although *cis* and *trans* forms of I should be possible, only one form was isolated. The diaddition product lost water very easily and rearranged to a phenol (II) which could be converted to the acetate (III). Hydrolysis of the acetate regenerated the phenol. This highly hindered phenol failed to give the spot test for hindered phenols.[8]



## Experimental[9]

The variations in the method of carrying out the reactions between the quinones and the organometallic reagents were the same as those which have been used in earlier studies and consisted of varying the proportions of the reactants, the time of reaction, the temperature and the method of combining the reactants. When the quinone was added to a solution of the organometallic compound, the latter was always in excess and diaddition products could be expected. When the organometallic compound was added to a solution of the quinone, the quinone was in excess at first and these conditions might be expected to give monoaddition products. The reaction mixture was decomposed with ice or with cold ammonium chloride solution. Slow evaporation of the

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(1) Presented at the Buffalo Meeting of the American Chemical Society, March, 1952.

(2) Taken in part from the M.S. theses of Martha Lumpkin and Marjorie McDonald.

(3) A. Willemart, *Bull. soc. chim.*, **9**, 83 (1942).

(4) H. M. Crawford, THIS JOURNAL, **70**, 1081 (1948).

(5) W. E. Bachmann, *ibid.*, **54**, 1969 (1932).

(6) S. F. Acree, *Am. Chem. J.*, **33**, 186 (1905).

(7) P. F. Oesper, C. P. Smyth and M. S. Kharasch, THIS JOURNAL, **64**, 937 (1942).

(8) G. H. Stillson, D. W. Sawyer and C. K. Hunt, *ibid.*, **67**, 303 (1945).

(9) Analyses for carbon and hydrogen by Beatrice Kent, analyst, of the University of California at Los Angeles.

ether layer gave solids which were recrystallized from ethanol or ethyl acetate.

When phenanthrenequinone was treated with phenyllithium the only addition product obtained was the known 9,10-dihydroxy-9,10-diphenyl-9,10-dihydrophenanthrene. The best yield (22%) was obtained when the ration of quinone to phenyllithium was 1:4 and when the suspension of the quinone in benzene was added to the solution of phenyllithium in ether and allowed to stand at room temperature for 30 minutes before being decomposed with ice. Standing overnight, refluxing the reaction mixture, or removing the biphenyl by steam distillation decreased the yield of the diol. Stirring during the addition of the quinone did not improve the yield. After most of the diol had been recrystallized, the remaining mother liquor gave a small amount of a white solid melting at 183–184° which depressed the melting point of the diol from 180–181° to 158–168°. This compound was apparently not an acetal or an ether, for refluxing it with hydrochloric acid in dioxan failed to give any ethanol. Analyses (by H. M. C.) gave 80.16% C and 6.77% H and a molecular weight of 344 in benzene.

When the proportions of 2,5-di-*t*-butyl-1,4-benzoquinone to phenyllithium were 1:1 or 1:2, large amounts of the quinone were recovered and the yields of I were 13–34%. The best yields were obtained when the proportion of quinone to phenyllithium was 1:8, when the quinone was added to the phenyllithium, and the mixture was either refluxed for 45 minutes or allowed to stand for one hour before being decomposed with a solution of ammonium chloride. Under these conditions the yields were 54–63%.

**2,5-Di-*t*-butyl-1,4-diphenylcyclohexadiene-2,5-diol-1,4 (I).**—This substance resulted from the reaction of either phenyllithium or phenylmagnesium bromide with 2,5-di-*t*-butyl-1,4-benzoquinone. It did not decolorize a solution of bromine in carbon tetrachloride, and was recovered unchanged after ozonizing 2 g. in chloroform for 45 minutes. All of the material was recovered as a mixture of I and II after boiling 1 g. for 17 hours with potassium permanganate and potassium carbonate. Oxidation with chromium trioxide in glacial acetic acid gave a small amount of benzoic acid. Refluxing 1 g. for four hours with potassium permanganate and dilute sulfuric acid resulted in converting 76% of it to II. Dehydrating I by boiling for two hours with Lucas reagent gave 88% of II, while boiling with glacial acetic acid for two hours gave a quantitative conversion to II. I melted at 236–238° after recrystallization from ethanol or ethanol and ethyl acetate.

*Anal.* Calcd. for $C_{26}H_{32}O_2$ (376): C, 82.94; H, 8.57. Found: C, 82.82; H, 8.73; mol. wt. in bromoform, 367.

**2,4-Diphenyl-3,6-di-*t*-butylphenol (II).**—This phenol was formed by the dehydration and rearrangement of I, the best procedure being the refluxing of a solution of I in glacial acetic acid for two hours. On cooling, the phenol crystallized from the acetic acid. It could also be recrystallized from a mixture of ethanol and ethyl acetate and melted at 208–209°. It did not decolorize a solution of bromine in carbon tetrachloride and gave no test for hindered phenols.[8] Ozonization of 1.5 g. of II in chloroform for 45 minutes gave 30% of unchanged II and a small amount of oil. It was recovered unchanged after boiling for 23 hours with aqueous potassium permanganate. Treatment with phenyllithium resulted in the recovery of 92% of the starting material. Reaction with methylmagnesium iodide gave a vigorous evolution of gas, and treatment of the remaining solution with acetyl chloride gave III.

*Anal.* Calcd. for $C_{26}H_{30}O$: C, 87.10; H, 8.43. Found: C, 86.77; H, 8.45.

**2,4-Diphenyl-3,6-di-*t*-butylphenyl Acetate (III).**—The acetate of the phenol was prepared by treating 1.8 g. of II with six times the theoretical amount of methylmagnesium iodide, and after the vigorous evolution of methane had ceased, refluxing the remaining solution for four hours with 10 ml. of acetyl chloride. Excess acetyl chloride and ether were removed by distillation and the resulting solid was recrystallized from methanol. It melted at 173–175°. The acetate was readily hydrolyzed to the phenol by boiling it with a solution of sodium in 95% ethanol.

*Anal.* Calcd. for $C_{28}H_{32}O_2$: C, 83.95; H, 8.05. Found: C, 83.65; H, 8.26.

**2,5-Di-*t*-butylhydroquinone (IV).**—The hydroquinone was prepared by refluxing 5 g. of the quinone with excess zinc dust and 80% acetic acid. The solution changed from yellow to red to colorless, and the known hydroquinone separated on cooling the filtered solution. It melted at 213–214° and the yield was 95%. The red color may have been due to the presence of a quinhydrone, but attempts to isolate the quinhydrone by crystallizing mixtures of the quinone and hydroquinone resulted in the two compounds coming out separately. The hydroquinone also resulted when the quinone (0.02 mole) was added to 0.08 mole of phenylmagnesium bromide. The mixture was decomposed with ammonium chloride solution after being refluxed for 90 minutes. Steam distillation of the mixture gave 30–32% of biphenyl, and the residue gave 43–51% of the hydroquinone.

**Diacetate of 2,5-Di-*t*-butylhydroquinone (V).**—The diacetate was prepared in 67% yield by reductive acetylation of the quinone, using zinc dust and acetic anhydride, and in 32% yield by treating the hydroquinone with phenylmagnesium bromide, followed by acetyl chloride. It was recrystallized from chloroform and melted at 172–173°.

*Anal.* Calcd. for $C_{18}H_{26}O_4$ (306): C, 70.56; H, 8.55. Found: C, 70.35; H, 8.58; mol. wt. in bromoform, 297.

The senior author wishes to thank the Tennessee Eastman Company for the 2,5-di-*t*-butyl-1,4-benzoquinone used in this study. She also wishes to thank the University of California at Los Angeles for the privilege of working in the laboratory of the Department of Chemistry during the second semester of 1950–1951.

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