with sodium methoxide to give ultimately a 1,3-diketone (VII) via the methyl enol ether VI. On the other hand, the nitrocyclopropylcarbinol is unaffected by action of sodium methoxide. Hence, it has been established that an electron attracting group, such as a carbonyl group, in position 1, plays an essential role in the reaction whereby such 2-nitrocyclopropyl compounds are converted into 1,3-diketones, via the enol ethers, by reaction with sodium methoxide.

3. A mechanism for this transformation has been suggested; this mechanism involves an unsaturated nitro ketone as an intermediate. Such a nitro ketone has been synthesized and subjected to the action of sodium methoxide, and it is shown that, in harmony with the suggested mechanism, the product is a substance which, by action of dilute acid, gives a 1,3-diketone.

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

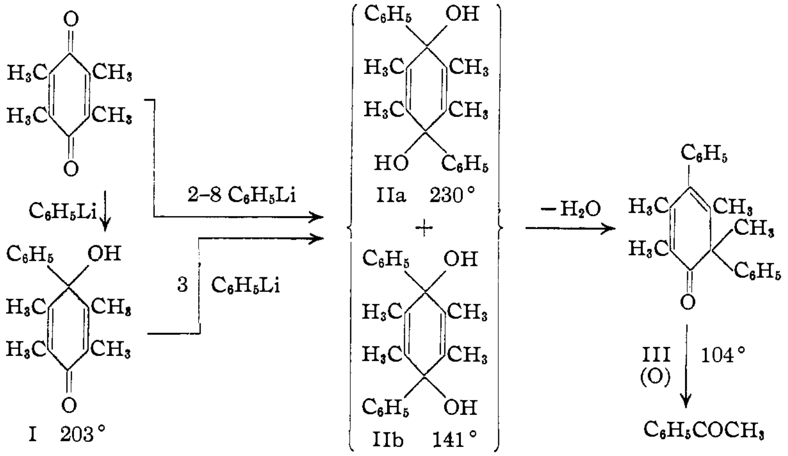
The Reaction between Duroquinone and Phenyllithium[1]

BY H. MARJORIE CRAWFORD AND MARJORIE MCDONALD[2]

This paper continues the series of studies[3] on the reactions of quinones with phenylmagnesium bromide and with phenyllithium. The first reaction studied, between duroquinone and phenylmagnesium bromide,[3a] gave a great variety of mono- and di-addition products, reduction products and double compounds, which accounted for only 20% of the quinone used. In later studies on other quinones[3c,e] it was shown that phenyllithium was useful because of its preferential addition to the carbonyl group, even in the presence of a conjugated system. In one case[3e] over 90% of the 1,2-1,2-di-addition product was obtained. With this excellent yield in mind, it was decided to see whether the 1,2-addition products could be obtained from phenyllithium and duroquinone, since phenylmagnesium bromide and duroquinone gave mainly the 1,4-addition products.

The reaction between phenyllithium and duroquinone took place readily and either the mono- or the di-addition products resulted, depending on the relative amounts of the reactants. Biphenyl could be isolated by steam distillation of the reaction products. Variations of the conditions of the reaction, such as mode of addition of the reactants, length of time before decomposition, and heating, seemed to have little effect on the results. When the ratio of phenyllithium to quinone was 1:1 the product was the mono-addition compound. A ratio of 2–8:1 gave the di-addition products. The mixture of di-addition products was also formed when an excess of phenyllithium (3:1) reacted with the mono-addition compound.

The relationships between the various compounds are shown in the chart.



The yields of I varied from 10–30%, while the best yield of this compound from phenylmagnesium bromide and duroquinone was 2.7%.[3a] IIa and IIb were formed in about equal amounts; the total yield varied from 20–57% when starting with the quinone and was 90% when starting with I. IIa and IIb are apparently a pair of geometric isomers and the *cis* configuration is suggested for the one which is more soluble and has the lower melting point. Both of these substances lose water readily when warmed with Lucas reagent and give the same compound (III), which was shown, by oxidation, to have a phenyl and a methyl group on the same carbon atom. This behavior parallels that shown by similar 1,4-diols.[3c,e]

In connection with this pair of isomers, it is interesting to remember that one of the products of the reaction between phenylmagnesium bromide and duroquinone also exists in stereoisomeric forms.[4]

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(1) Abstract from a thesis by Marjorie McDonald, presented in partial fulfillment of the requirements for the degree of Master of Science at Vassar College in 1948.

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(3) (a) Smith and Crawford, THIS JOURNAL, **50**, 869 (1928); (b) Crawford, *ibid.*, **57**, 2000 (1935); (c) **61**, 3310 (1939); (d) **63**, 1070 (1941); (e) **70**, 1081 (1948).

(4) Crawford, *ibid.*, **56**, 1803 (1934).

Decomposition of the lithium complex with acetyl chloride gave a dark oil from which the only products isolated were small amounts of biphenyl, duroquinone, and, in one case, IIa. No acetyl derivatives of I or II were ever found and it is interesting to note that the reaction of phenylmagnesium bromide with duroquinone, followed by decomposition of the magnesium complex with acetyl chloride, gave acetyl derivatives of the mono- and di-addition products which were formed by 1,4-addition, while no acetate of I was ever detected.

Experimental

Preparation of Duroquinone.—Duroquinone was prepared according to the method described by Smith.[5]

Preparation of Phenyllithium.—The method used in the preparation of this reagent was essentially that of Gilman, Zoellner and Selby[6] with the omission of the nitrogen train. The concentration of the phenyllithium was determined by titration with standard hydrochloric acid before its use in the earlier reactions. After it became apparent that the yield of II was not affected by other variations, so long as there was a substantial excess of the phenyllithium, this titration was omitted.

Procedure.—Several variations in the procedure were tried in order to determine the best conditions for the formation of the various solid products. The method of mixing the reactants (adding a solution of duroquinone to a solution of phenyllithium or adding a solution of phenyllithium to a solution of duroquinone) did not vary the results. Refluxing the reaction mixture decreased the yield slightly, but the length of time elapsing before the decomposition of the lithium complex made no difference. Decomposition of the reaction mixture with acid reduced the yields, but water or ammonium chloride solution were equally satisfactory. From about twenty reactions, carried out under varying conditions, it was shown that the highest yield of solid products was obtained by allowing the reaction mixture to stand at room temperature for a short time, then decomposing it with water and allowing the ether layer to evaporate slowly at room temperature. When solid appeared, it was filtered, washed with diisopropyl ether and crystallized from ethanol or from a mixture of benzene and petroleum ether (60–70°). When the ratio of phenyllithium to duroquinone was 1:1, the main product was 10–20% of I. When the ratio of phenyllithium to duroquinone was 2–8:1, the solid consisted of a mixture of IIa and IIb. A ratio of 5:1 gave the best yields, about 20–57%. The 230° isomer, IIa, was less soluble and separated first when the mixture was crystallized from ethanol. IIb was much more soluble and separated after adding a little water to the ethanol solution.

2,3,5,6-Tetramethyl-1-phenylcyclohexadiene-2,5-one-4-ol-1, I, m. p. 203°, was obtained in 10–20% yields when one mole of phenyllithium and one mole of duroquinone reacted. It was identical with the material obtained in 2.7% yield from the reaction between duroquinone and phenylmagnesium bromide.[3a]

2,3,5,6-Tetramethyl-1,4-diphenylcyclohexadiene-2,5-diol-1,4, IIa, m. p. 230–232°, was obtained in 45% yield from the reaction of phenyllithium on I, and in yields of 10–30% when phenyllithium reacted with duroquinone.

Anal. Calcd. for $C_{22}H_{24}O_2$ (320): C, 82.46; H, 7.55. Found: C, 82.46, 82.07; H, 7.54, 7.34; mol. wt., 310 (Rast).

IIa crystallized from ethanol as transparent, colorless, square plates. It is very soluble in acetone, ethyl acetate and benzene and only slightly soluble in petroleum ether.

When 0.43 g. of IIa was boiled for two hours with 10 ml. of benzene and 5 ml. of Lucas reagent, it was dehydrated to give 0.15 g. (37%) of III. The procedure is described under compound III.

2,3,5,6-Tetramethyl-1,4-diphenylcyclohexadiene-2,5-diol-1,4, IIb, m. p. 141.5–142.5°, was formed along with IIa in about equal amounts and separated from the original ether solution after most of the IIa had crystallized. It crystallized from a mixture of ethanol and water as cottony, white needles.

Anal. Calcd. for $C_{22}H_{24}O_2$ (320): C, 82.46; H, 7.55. Found: C, 82.84, 82.38; H, 7.45, 7.68; mol. wt., 322.

A solution of 2 g. of IIb in 50 ml. of benzene was boiled for four hours with 15 ml. of Lucas reagent. The benzene layer was washed with water and with sodium bicarbonate solution, filtered and evaporated to dryness. The solid, recrystallized from petroleum ether (60–70°), amounted to 1.75 g. (93%) of III.

A solution of 0.9 g. of IIb in acetone decolorized 1.55 g. of potassium permanganate. No acid products could be isolated from this oxidation and the neutral portion reacted with semicarbazide to give 0.15 g. of white solid, m. p. 135–137° which was not identified. The same product was obtained from the oxidation of III.

2,3,5,6-Tetramethyl-1,3-diphenylcyclohexadiene-1,5-one-4, III, m. p. 104–107°, resulted from the dehydration and rearrangement of either IIa or IIb. It is more soluble than any of the hydroxy compounds and can be crystallized from 50% ethanol, methanol or petroleum ether as pale yellow, transparent, stout needles. Occasionally clear, yellow chunks would separate from the solutions and melt around 130–135°. When these were recrystallized, the melting point would again be around 104°. The per cent. of carbon and of hydrogen was the same, regardless of the melting point.

Anal. Calcd. for $C_{22}H_{22}O$ (302): C, 87.38; H, 7.34. Found: C, 87.63, 87.10; H, 7.54, 7.37; mol. wt., 288.

A solution of 0.6 g. of III in acetone decolorized 1.25 g. of potassium permanganate. No acid products could be isolated, and the neutral fraction reacted with semicarbazide to give 0.1 g. of white solid melting 135–137°, identical with the corresponding compound from the oxidation of IIb. This compound has not been identified.

III was recovered unchanged from treatment with semicarbazide.

When 1 g. of III was refluxed for four hours with 3 g. of potassium dichromate and 20 ml. of glacial acetic acid, no acid products were isolated but the neutral fraction gave the semicarbazone of acetophenone, identical with a known sample.

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Summary

1. Phenyllithium reacts with duroquinone to give a 1,2-addition product when the reactants are used in equivalent quantities.

2. When an excess of phenyllithium is allowed to react with duroquinone, two stereoisomeric 1,2-1,2-diaddition products are formed in approximately equal amounts.

3. Both of these geometric isomers lose water easily, and form the same compound.

4. Structures are proposed for three new compounds.

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(5) "Organic Syntheses," Coll. Vol. II, 248, 254 (1943).

(6) Gilman, Zoellner and Selby, THIS JOURNAL, 54, 1957 (1932).