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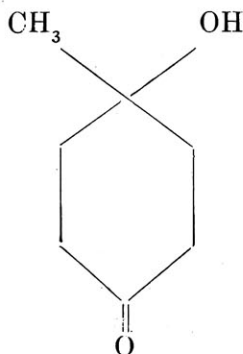
SESSION OF 1909-1910

THE ACTION OF ORGANO-MAGNESIUM COMPOUNDS ON QUINONE.

—By CURTIS C. WALLACE.*

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It is generally known that quinone has properties common to both a diketone and a peroxide, but it differs, however, from the former in being a powerful oxidizing reagent and from the latter in forming an oximide compound with hydroxylamine. It is also known that diketone¹ with Grignard's reagents undergoes the pinacone condensation yielding the corresponding pinacone. Further, Bamberger and Blangey² obtained a quinol of the structure



with methyl magnesium iodide from toluquinone and xyloquinone, but were unable to get the same from quinone. In

* Contributions from the Science Laboratories of Dalhousie University [Chemistry].

¹ Zelinsky, Ber. d. deutsch. chem. Ges. **35**, 2138, (1902).

² Bamberger u. Blangey, Ber. d. deutsch. chem. Ges. **36**, 1625, (1903).

the following investigation I have endeavored to study more minutely the behaviour of quinone with Grignard's reagents, methylmagnesium iodide, ethylmagnesium bromide and phenylmagnesium bromide.

EXPERIMENTAL.

Quinone and Methylmagnesium Iodide.

5 grams of clean magnesium ribbon were placed in a 500 c.c. flask. The flask was fitted to a reflux condenser, and 30 grams of methyl iodide, dissolved in 40 grams of absolute ether, slowly added through the condenser. Immediately a reaction set in, which was moderated by cooling the flask. When the reaction was about complete, the flask was warmed on a water-bath for an hour. An ethereal solution of 10 grams of quinone was then added, 5 c.c. at a time, with constant shaking, waiting each time until the reaction somewhat abated. The saturation point was obtained by noting when no precipitate formed on the addition of the quinone solution to a test-tube containing a portion of the ethereal solution taken from the flask. On addition of quinone, a violent reaction took place, accompanied by a cracking noise; the reaction product precipitated as a green amorphous mass insoluble in ether. With the object of moderating the reaction, the experiment was repeated, the ethereal solution being this time kept in a freezing mixture (-8°C), with, however, the same results as obtained at ordinary temperature; one molecule of quinone united with two molecules of methylmagnesium iodide. The methylmagnesium iodide quinone compound was found impossible to isolate; it was either insoluble or the solvent caused decomposition.

After allowing the quinone mixture to stand over night, 75 c.c. of cold water and dilute hydrochloric acid enough to acidify the solution were added. No change of colour was apparent on addition of the water, but the acid changed the mixture brown and precipitated a brown flocculent precipitate.

This precipitate was filtered, washed with ether in which it was insoluble, and dried on a filter-paper. The brown powder remaining readily dissolved in ethyl and methyl alcohols and acetone, forming a brown solution, which on evaporation left a black enamel-like residue. It was insoluble in water, and all other common organic solvents, but those mentioned above. It was impossible to obtain it in a crystalline form, but a precipitation of it was obtained by adding water to a concentrated alcoholic solution and evaporating until little or no alcohol remained. This process was not satisfactory, as the compound separated as a colloid in pure water. This substance was not further studied. The total yield from the experiment was only about 0.5 gram.

On evaporating the ethereal solution in a porcelain dish, there remained a green crystalline substance in the central part, with a brown amorphous mass surrounding it. The crystals were removed and in order to obtain more of them the amorphous mass was redissolved in ether and again evaporated. This mechanical process of separation was repeated until a quantity of the crystals was obtained. They were recrystallized from ether and a pure-looking product obtained with a practically constant melting point of 170°C.

An analysis gave the following results :

0.1501 gram of substance gave 0.3646 gram CO₂ and 0.0609 gram H O.

	Calculated for C ₁₂ H ₁₀ O ₄ .	Found. I
C	66.02%	66.29%
H	4.63%	4.51%

The green crystals gave tests for a quinhydrone; the analysis prove it to be of the formula C₁₂H₁₀O₄, or ordinary quinhydrone.

The remaining amorphous tarry residue left from the ether solution consisted of free iodine, some quinhydrone and re-

duction products of the reaction. It was fairly large in quantity, but it was not practicable to isolate any other pure product from it.

Quinone and Ethylmagnesium Bromide.

An ethereal solution of 11 grams of quinone was added gradually, 5 c.c. at a time, to a solution of ethylmagnesium bromide obtained by dissolving 5 grams of magnesium ribbon in 25 grams of ethyl bromide and 50 grams of absolute ether. To ensure a more complete reaction, the mixture was allowed to stand a day with occasional shaking. The blue reaction product which separated out insoluble in ether, was treated with ice water and acidified with dilute hydrochloric acid. The addition of water turned the mixture green, while a further addition of acid turned it brown, separating out at the same time, as in the case of the methyl iodide compound, a brown precipitate insoluble in ether or water. It was observed that although the ethylmagnesium bromide quinone compound was blue, the mixture, after the addition of water, was green and that no such change of colour was noticed with the iodide quinone compound. This was probably due to the fact that both the iodide quinone compound and its products of decomposition were green. Moreover, it was found that the amorphous precipitate, insoluble in ether, was readily soluble in alkalis, producing a green solution; and since magnesium hydroxide, which would be produced by the addition of water, is slightly soluble in water, it would dissolve enough of the substance to colour the mixture green.

The acidified mixture was then filtered and the amorphous precipitate remaining on the filter paper was washed with dilute hydrochloric acid and then with ether and dried. The ethereal solution was next separated and the water solution further extracted with ether. On a partial evaporation of the ether a solid separated, which was filtered and recrystallized from ether. The substance gave practically a constant melt-

ing point of 171°C. Analysis of the substance gave the following results:

I. 0.1326 gram of substance gave 0.3219 gram of CO₂ and 0.0548 gram of H₂O.

II. 0.1336 gram of substance gave 0.3224 gram of CO₂ and 0.0597 gram H₂O.

	Calculated for	Found.		
	C ₁₂ H ₁₀ O ₄ .	I	II	Mean
C	66.02%	66.21%	65.82%	66.01%
H	4.63%	4.59%	4.96%	4.77%

The sample was pure quinhydrone.

The remaining residue left from evaporation of the remainder of the ethereal solution contained more quinhydrone and a brown tarry decomposition product, but no evidence of any free halide as was the case with the methyl-iodide residue.

The brown powder, obtained from the residue washed in ether, was then further extracted with ether free of alcohol until nothing remained in it that was soluble in ether. It was next boiled in 100 c.c. of water, filtered and washed with water. When dry, it was dissolved in alcohol, filtered and the alcohol evaporated off. A shining black enamel-like residue remained, which decomposed at a very high temperature. When dried in a hot-air closet for two hours at 125°C., analyses gave the following results:

I. 0.1620 gram of substance gave 0.3876 gram CO₂ and 0.0682 gram of H₂O.

II. 0.1560 gram of substance gave 0.3702 gram CO₂ and 0.0678 gram of H₂O.

A slight residue remained after each combustion, but nothing of appreciable weight.

	Calculated for	Found.	
	empirical formula C ₆ H ₅ O ₂	I	II
C	66.02%	65.25%	65.88%
H	4.63%	4.67%	4.89%

The compound was extremely hygroscopic. An analysis of the same sample as analysed above, but before the continued drying at high temperature, gave the following results:

0.1298 gram of substance gave 0.2876 gram CO_2 and 0.0619 gram H_2O .

C	60.42%
H	5.29%

The total yield was about 10 per cent of the quinone used. The colour of a concentrated alcoholic solution of this substance is dark brown; one cubic centimeter of this concentrated solution added to 200 c. c. of water is pink; and the addition of a drop of any alkali gives a grass green, while a drop of acid will restore the pink again. This substance reduces an alkaline solution of potassium permanganate, and is apparently oxidized by adding bromine water to an alcoholic solution of it. By either of these treatments an amorphous product with a light yellow colour was obtained.

A method of precipitation of this same substance was developed. About 0.4 gram of the same sample as analysed above, was dissolved in a few cubic centimeters of sodium hydroxide and diluted with water to one liter. The green solution was heated to boiling, acidified with strong hydrochloric acid and then the brown precipitate thus formed allowed to settle. A tall cylindrical jar was used, as it offered a smaller bottom surface and a greater column of water, thus making it possible, when the precipitate had settled, to syphon the solution off, leaving but little with the precipitate. The precipitate was heated again with another liter of dilute hydrochloric acid, 10 volumes of water to 1 volume of acid, Sp. G. 1.2, and allowed to settle. The decantation was repeated three times with the same quantity of dilute acid each time. The fourth dilution was filtered while hot through a hot-water funnel and washed thoroughly with hydrochloric acid of the same dilution as above, the last washing being with

pure water. When dried as much as possible with a suction-pump, it was heated while still on the filter-paper in a hot-air closet for three hours at 125°C. As the precipitate adheres so closely to the filter paper, a suction pump and a platinum cone are practically indispensable in carrying out the above filtration. The brown mass was then removed from the filter paper, dissolved in ethyl alcohol and filtered. On evaporation of the alcohol, the remaining residue was the same as obtained by the other method. An analysis gave the following results:

(The same analyses of the substance as given above, are also given here for comparison.)

0.1492 gram of substance gave 0.3605 gram CO₂ and 0.0598 gram of H₂O.

	Calculated for	Found.	Former Analyses.	
	C ₆ H ₅ O ₂ .		I	II
C	66.02%	65.89%	65.25%	65.88%
H	4.63%	4.45%	4.67%	4.89%

Quinone and Phenylmagnesium Bromide.

An ethereal solution of 6 grams of quinone was added gradually to a solution of phenylmagnesium bromide obtained by dissolving 3.5 grams of magnesium ribbon in 25 grams of brombenzene and 40 grams of absolute ether. On standing for a day, 75 grams of water and dilute hydrochloric acid, enough to acidify the mixture, were added. The brown precipitate produced was filtered off and the ethereal solution separated as in the former compounds. The precipitate was washed with hot water, then ether, and left to dry. The residue left from dissolving in and evaporating from ethyl alcohol was small. Its properties were similar to the compounds obtained from methyl iodide and ethyl bromide. The product obtained from phenyl bromide and methyl iodide has not yet been analysed. The pure substance, however, could

be obtained easily enough by following either of the methods of procedure described in the separation of the ethyl bromide compound, preferably the hydrochloric acid precipitation method, and the analysis thus procured if materials or time allowed.

On a partial evaporation of the ethereal solution, a quantity of quinhydrone crystallized, which was filtered and recrystallized from ether. It had a practically constant melting point of 170°C .

Analyses gave the following results :

I. 0.1372 gram of substance gave 0.3330 gram CO_2 and 0.0584 gram H_2O .

II. 0.1224 gram of substance gave 0.2984 gram CO_2 and 0.0531 gram H_2O

	Calculated for	Found.		
	$\text{C}_{12}\text{H}_{10}\text{O}_4$	I	II	Mean
C	66.02%	66.19%	66.48%	66.33%
H	4.63%	4.73%	4.82%	4.77%

The carbon and hydrogen were both too high. This was expected as the sample had a slight odour of diphenyl.

The residue remaining after the complete evaporation of the ether was extracted with 75 c.c. of carbon tetrachloride, 25 c.c. at a time. The carbon tetrachloride was then distilled off and there remained in the flask a product which did not boil until the temperature nearly reached 250°C . The portion distilling from 250 - 260°C . solidified in the condenser tube was collected and crystallized from alcohol. The product consisted of transparent lustrous plates which had a constant melting point of 70°C . An analysis gave the following results, which prove it to be diphenyl.

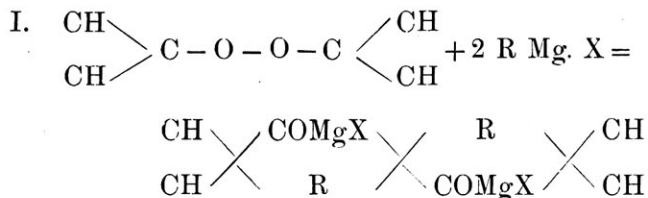
0.1210 gram of substance gave 0.4143 gram CO_2 and 0.0731 gram H_2O .

	Calculated for	Found.
	$\text{C}_6\text{H}_5\text{C}_6\text{H}_5$	
C	93.45%	93.38%
H	6.55%	6.71%

The method of separation was by no means complete, but nearly 2 grams of diphenyl were obtained.

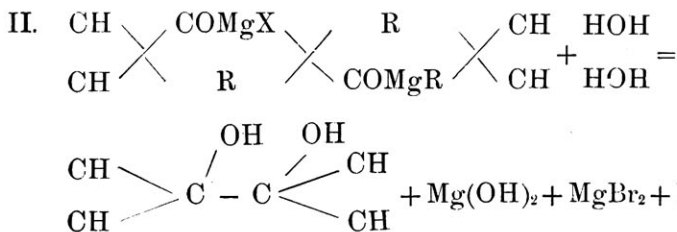
DISCUSSION.

The organo-magnesium halide quinone compounds, which form with such energy on the addition of quinone to the organo-magnesium halide, are not stable, but decompose when exposed to the air. The bromide is blue and the iodide is green. Their formation is possibly in accordance with the following equation :

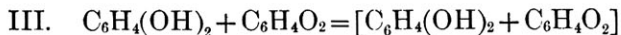


Two molecules of the organo-magnesium halide are used to each molecule of quinone.

The formation of the quinhydrone may be explained by the production first of hydroquinone, as shown in the following equation :



The hydroquinone then reacts with the unattacked quinone, the reaction being expressed by the following equation :



The production of diphenyl in the action of phenylmagnesium bromide quinone is evidence in support of the reaction as given in equation II.

The investigation of the compound having the empirical formula C_6H_4O obtained from the action of ethylmagnesium bromide on quinone is proceeding; as indicated in the experimental part, similar and probably identical compounds were obtained from methylmagnesium iodide and phenylmagnesium bromide, but until further study has shown the nature of this substance, nothing definite can be stated of the part it plays with regard to the reaction.

No pinacone has been obtained, and no quinol of the structure obtained by Bamberger and Blangey.

These experiments were carried out in the laboratories of Dalhousie University and were suggested by Professor E. Mackay, and I wish, in conclusion, to thank him for the suggestions, helpful criticisms and kindness offered during the progress of the work.

Chemical Department, Dalhousie University,
Halifax, N. S., April 15, 1910.