6-1963

Addition reactions of quinones

Herman Helber
Union College - Schenectady, NY

Recommended Citation

Helber, Herman, "Addition reactions of quinones" (1963). *Honors Theses*. 1924.
https://digitalworks.union.edu/theses/1924

ADDITION REACTIONS OF QUINONES

by

Herman Helber
III

****

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements for Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

MAY, 1963

ADDITION REACTIONS OF QUINONES

by

HERMAN HELBER

A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science with a major in Chemistry.

By Herman Helber

Approved By William B. Martin, Jr.

May 24, 1963

Acknowledgement

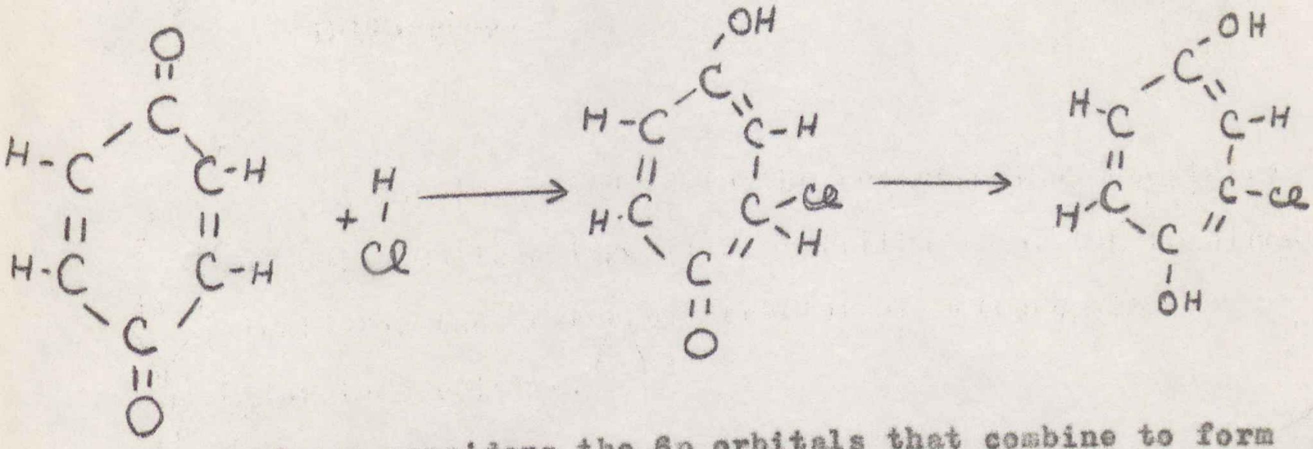
I wish to sincerely thank Dr. William B. Martin, Jr. of Union College for his inspiring aid on this project. His suggestions and continual encouragement were greatly appreciated.

CONTENTS

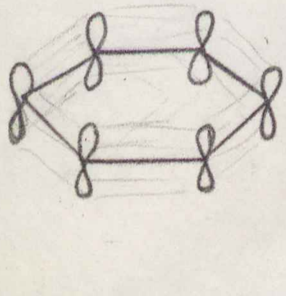
Introduction

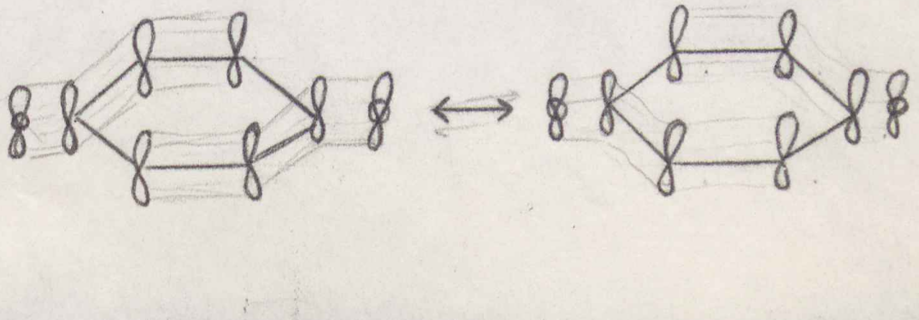
The general purpose of this project has been to obtain a knowledge about the reaction of para-benzoquinone when irradiated with ultraviolet light in water or ethanol. The 1,4 benzoquinone, often called simply quinone, is a yellow crystalline solid melting at 116°C and having a sharp penetrating odor.

Since quinone does not completely behave like an aromatic compound, its reactions are of great interest. From th fact that quinones undergo 1,4 additions, such as the reaction of hydrogen chloride with quinone, one could consider them to be a type of α,β unsaturated cyclic hetone. (1)



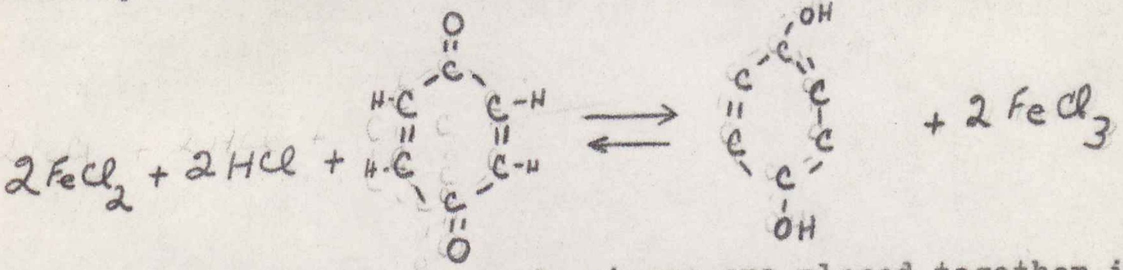
If one considers the 6p orbitals that combine to form 6π orbitals, as in benzene, one could consider the quinone to be aromatic in nature. The difference between the benzene and the quinone, from this point of view, is that the p orbitals of the oxygens adjacent to the ring also enter into the formation of the π orbitals. (6)





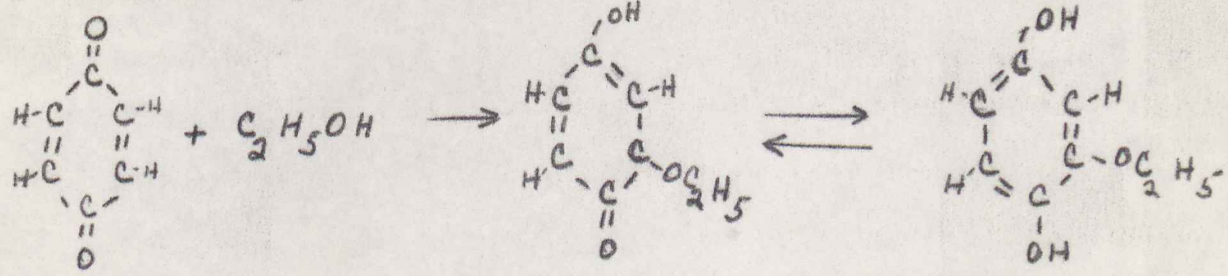
From the " streamer pictures" indicated above, it can be seen how the addition of the two oxygens changes th nature of the aromaticity and how the symmetry of the molecule makes 1,4 addition possible.

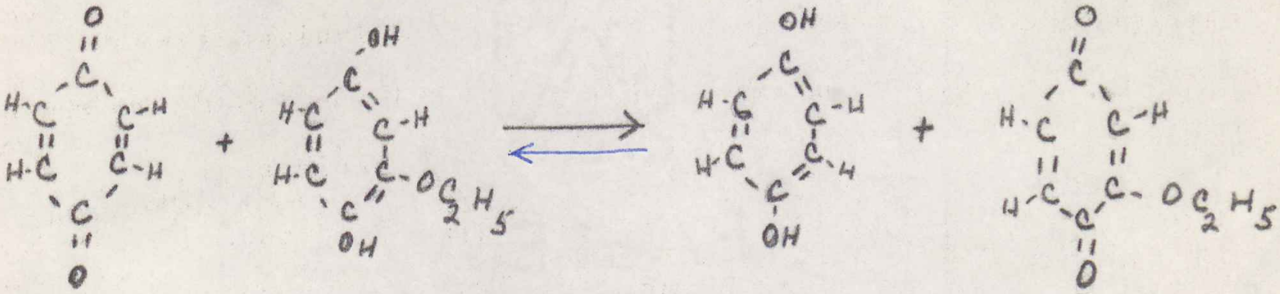
It is interesting to note that although chemical reactions indicate quinone to be an aliphatic ketone, it is formed by the oxidation of an aromatic compound and forms an aromatic compound on reduction. A reduction product that seems to be present in most reactions involving quinone is hydroquinone. One of the few reversible oxidation-reduction reactions that take place in organic Chemistry involves the reduction of quinone to hydroquinone.



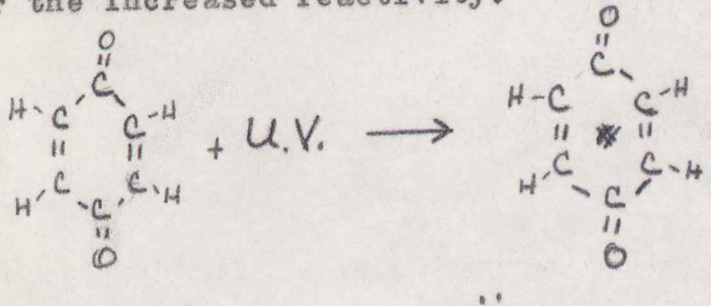
When hydroquinone and quinone are placed together in a solution they form the molecular compound, quinhydrone. This compound is a greenish crystalline solid. Although the exact nature of the valence forces is not known, it can be seen that the bond is not strong since the molecule is easily dissociated into its two constituents and since an infrared spectrum of the compound shows only the combined characteristics of the quinone and hydroquinone molecules.

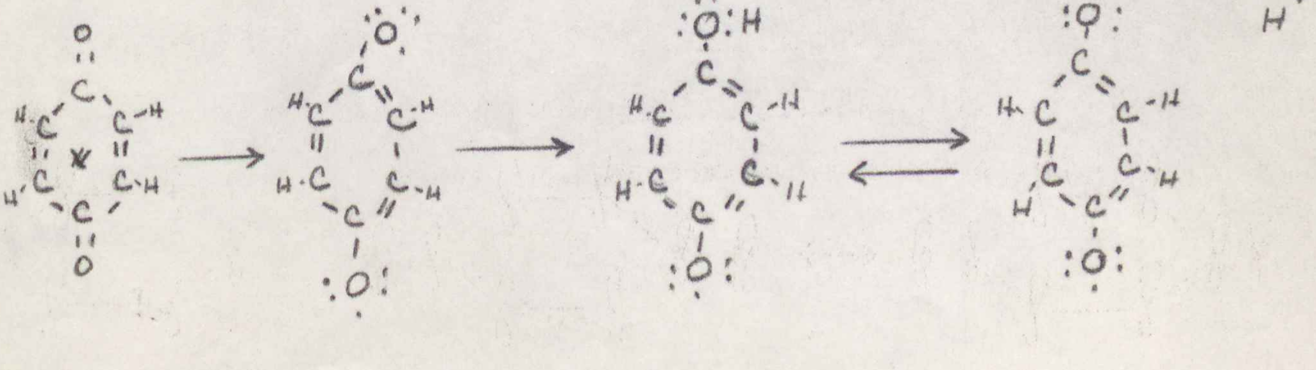
The specific purpose of this project has been to determine if an alkoxy-benzoquinone is produced when a solution of benzoquinone in alcohol is irradiated with ultraviolet light. Since we have 1,4 addition of water to excited benzoquine we might expect an alcohol to add similarity. This would lead to an alhoxyhydroquinone which would then be oxidized to an alhoxyquinone by excess benzoquinone.





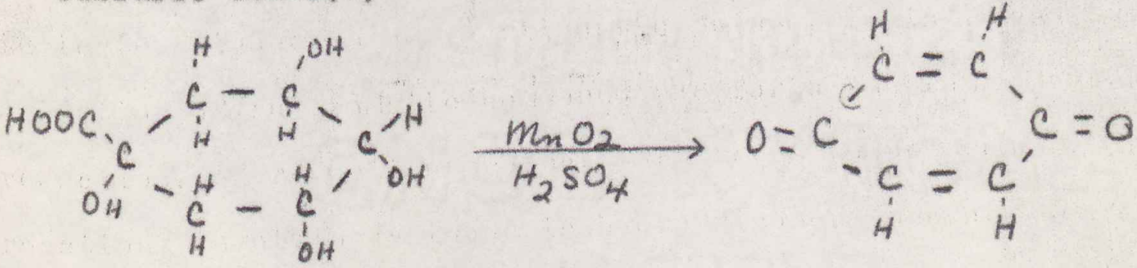
Quinone shows a marked increase in reactivity when it is irradiated with U.V. A possible explanation for this could be that the electrons in central carbon atoms of the quinone absorb quanta of energy. The resulting excited state could then lead to a free radical formation. This could account for the increased reactivity.





Historical

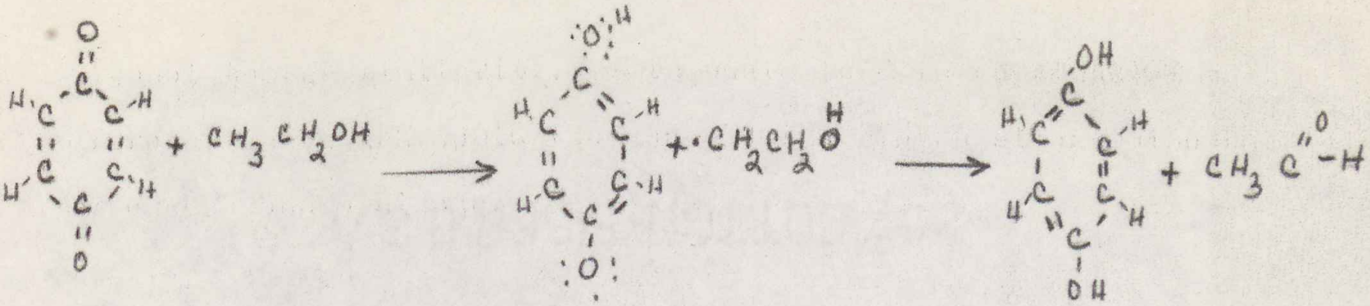
Quinone was discovered in 1838 as a product of the oxidation of quinic acid with manganese dioxide and sulfuric acid.(1)

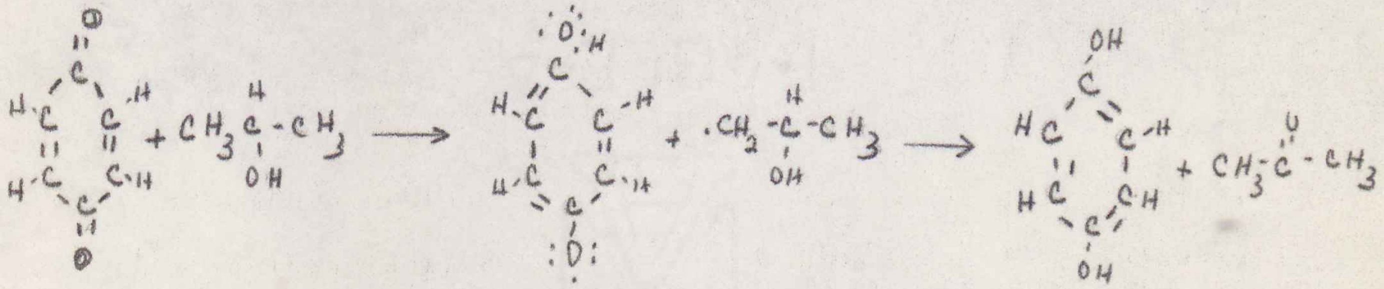


The quinic acid used in the reaction was obtained from cinchona bark. Its conversion into the quinone actually involves dehydration, decarboxylation and finally oxidation.

More than half a century passed, however, before any real interest was generated in this compound. In 1901 Silber investigated the reaction of quinone with various organic compounds.(8) The reactions of interest in connection with this project are those of ethanol and isopropyl alcohol with quinone. When a solution of quinone in ethanol was irradiated with U.V. the products observed were hydroquinone and acetaldehyde. A similar reaction carried out with isopropyl alcohol yielded, among other products, hydroquinone and acetone. The presence of quinone and hydroquinone in the same solution also results in the formation of quinhydrone.

In each case it seems likely that the mechanism for the reactions involves the abstraction of a hydrogen from the alcohol.

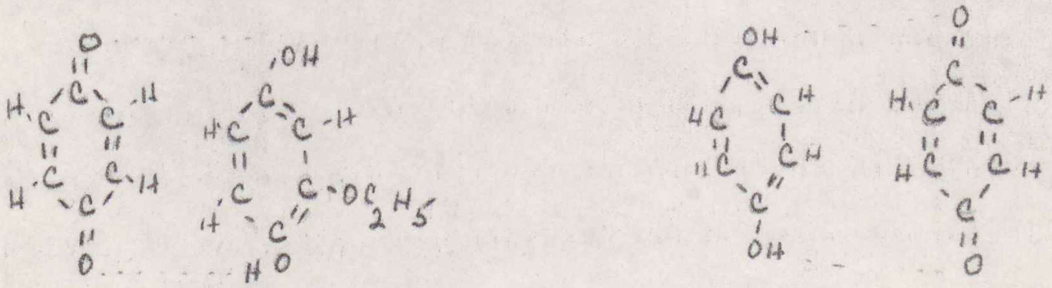




The free radical formed could then lose a free hydrogen atom from the carbon to which the hydroxyl group is attached. A tautomeric shift of the hydrogen would then produce acetaldehyde and acetone.

A few years after, Silber made the initial attempts at investigating the chemistry of quinones, while Hartley and Leonard made extensive studies of reactions by means of absorption studies.(8) They obtained the spectrum of pure quinone and hydroquinone in the vapor state and in solutions of water and ethanol. After solutions of quinone in water or ethanol had been irradiated for several hours, spectral studies were again made. The changes in the spectrum confirmed the decomposition of quinone. From the peaks observed, hydroquinone was definitely shown to be one of the products of the reaction.

It was also noted that a brownish substance was always formed when a solution of quinone in water or ethanol was irradiated. A combustion analysis indicated a possible structure of $C_{12}H_8O_5$ for the substance. This could be a dimer or polymer resulting from hydrogen bonding and electrostatic forces. It could result from any combination of quinone, hydroquinone and possible alhoxyquinones.



Possible dimers

The first hint about the hetonic nature of the quinone molecule came a few years later when Hartley and Little noticed that the spectrum of p. benzoquinone differed greatly from that of its benzoid derivatives.(4). They noted that there was always a weak absorption peak at 280 and 315 mμ. This is the absorption region for hetones. By combining benzoid and hetonic absorptions, the p. benzoquinone absorption bond was obtained. This would indicate the dual nature of the quinone mentioned earlier. The drawback in their observations is that no corrections were made for solvent effects. This would cause a shift in the absorption peaks.

Perhaps the most extensive investigation of the nature of quinones was done in 1929 by Leighton and Forbes.(2) They investigated the quantum efficiencies of various reactions and tested the effects of impurities in the reaction mixture.

It was shown that oxygen definitely retards the reactions of quinones in alcohol and water, having a greater effect on the former. The addition of acid or base retards the reaction in water but accelerates it in alcohol.

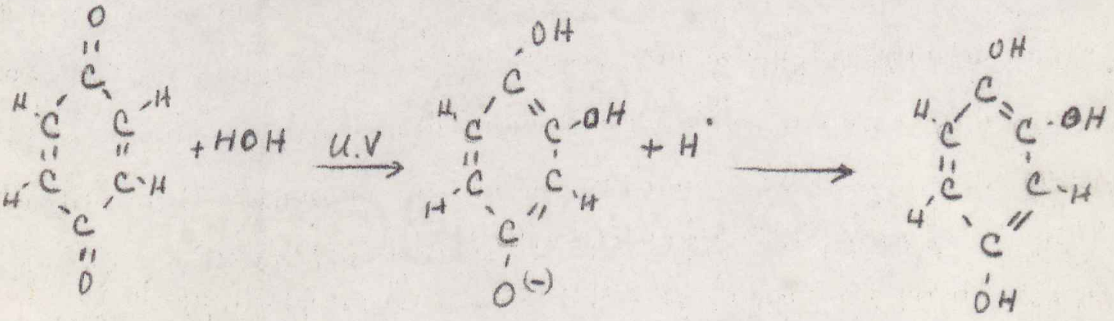
The quantum efficiency is the ratio of the number of molecules effected to the quanta absorbed. Although there are many complicated factors involved in calculating the quanta efficiencies, a rough estimate is still helpful. The quantum efficiencies for several reactions were obtained from the slope of a plot of quanta absorbed vs. molecules effected.

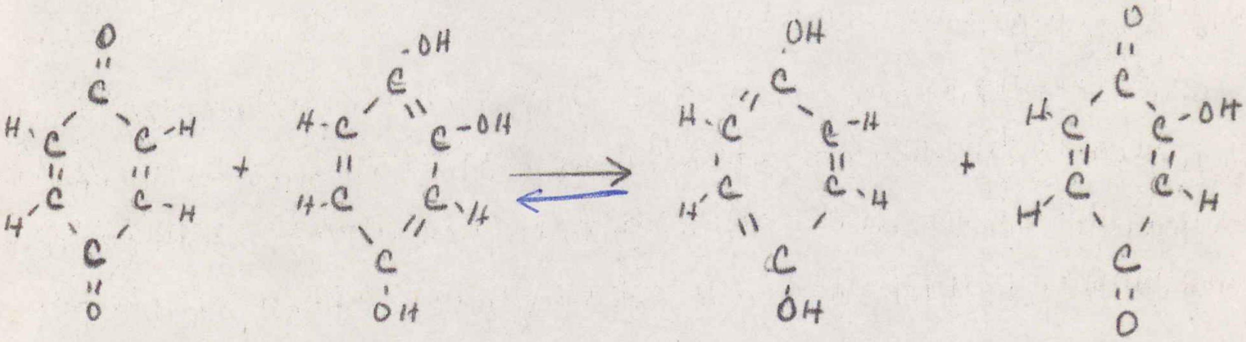
Quinone in water was irradiated until about twenty percent had reacted. The average quantum efficiency measured for this reaction was about 0.5 for irradiation wavelengths between 2537Å and 4350Å, decreasing above this value. Reactions of quinone in absolute ethanol and in 50% ethanol resulted in the same general quantum efficiency.

One reason for the 0.5 value of the quantum efficiency could be that one half of the energy, supplied by the photons, is necessary for correct orientation of the oxygens before reaction takes place. The second and favored reason could be that the efficiency is unity for the main reaction, but less than 0.5 for secondary reactions so that the overall efficiency is about 0.5.

As shown in previous works, hydroquinone and a brownish polymer again seem to be present in each reaction mixture.

The most accurate analysis of quinone reactions was carried out by Poupe.(7). He found, by polaroqraphic analysis, that benzoquinone in water when irradiated led to the formation of hydroxyhydroquinone. This 1,4 addition compound was reoxidized to hydroxybenzoquinone in excess quinone.





By following shifts in half wore potentials of the compounds in the reaction mixture he could accurately determine the rate of the reaction. The identification of the products was accomplished by comparing the half wove potentials of the unknown with half wove potentials of the pure knowns. Each of th e products mentioned above was thus definitely proven to be present.

Experimental

It was shown, as in many previous works, that a solution of quinone in water of alcohol darkened when exposed to light. When a clear solution was placed in an opaque container, it too darkened but at a perceptibly slower rate.

The first object of the experimental work was to obtain an adequate means for the identification of the various components present in the reaction mixture. Having these knowns labeled, we could then notice the presence of any other constituents. An attempt was made to obtain the spectrum of pure benzoquinone in ethanol and water by means of vapor phase chromatography. This was not successful. The alcohol and water peaks showed up immediately. No quinone peak was visible even after many hours. Many different columns were used with the same end result.

Thinking that the columns were perhaps too long for the quinone to pass adequately, columns of six, ten, and twelve inches were made. The fillings in these were carbowax 20 m and cromasorb w which had been melted together in a solution of methyl chloride. The results obtained were again negative. The pemperature of each run was 225°C. Helium was used as a carrier gas.

A possible explanation could be that the quinone polymerized on the column and then slowly diffused through.

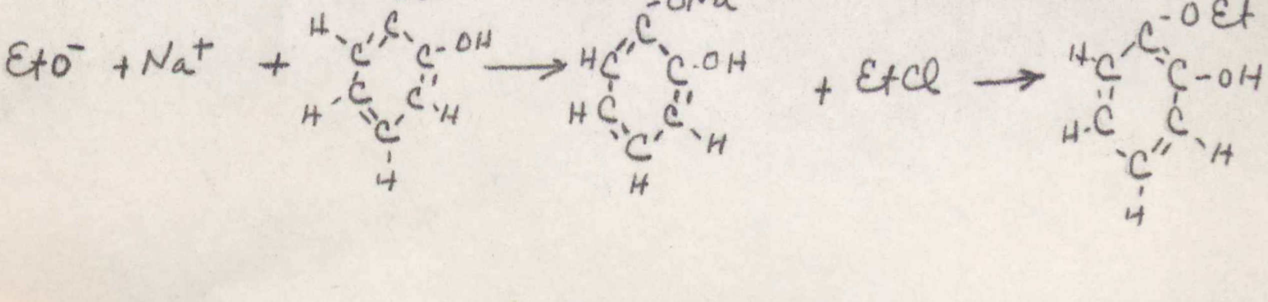
Column absorption chromatography was next tried as a means of seperation. As equal mixture of quinone and hydroquinone was added to the column. Ethyl alcohol was used as a solvent. With an automatic rotating device it was possible to obtain periodic twenty ml. samples of solution coming through the bottom of the column. The quinone and hydroquinone came over almost immediately. The quinhydrone, formed when the quinone was added to the hydroquinone, slowly disappeared from the top of the column. the disappearance of this greenish-black residue shows that it was separated into quinone and hydroquinone as it was adsorbed and desorbed while moving down the column. This shows the weak nature of the quinhydrone bond.

With adequate choice in polarity of solvents, it would seem that this should be a good means of separating the reaction mixture.

The synthesis of ethoxy-benzoquinone was next attempted.

To 100 ml. of absolute ethanol was added, in small amounts, one half molecule of sodium metal. After reaction was complete, the same amount of catechol (mp.=105°C), dissolved in ethanol, was added to the mixture. A cooled solution of one half molecule of ethyl chloride in ethanol was then added. The reaction mixture was stirred for several minutes. The final mixture consisted of a yellowish solution and of a white precipitate which was assumed to be soduim chloride.

$$EtOH + Na \rightarrow EtO^- + Na^+ + \tfrac{1}{2}H_2\uparrow$$



The solution was drawn off and distilled. A very small amount of black residue was the only product. The white precipitate, which I had assumed to be sodium chloride and had thus discarded, apparently was composed of sodium catecholate.

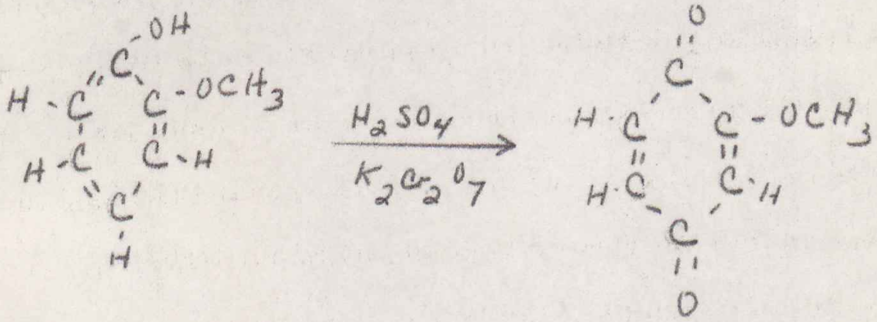
A second reaction was carried out. This time the liquid was drawn off and the remaining solid acidified to hopefully give ethoxy phenol. The aqueous solution was extracted with ether. Upon evaporation of the ether, brownish crystals were obtained with a relatively high yield. These crystals melted at 98-102°C. An infrared spectrum confirmed the suspicion that the crystals were the starting material, catechol.

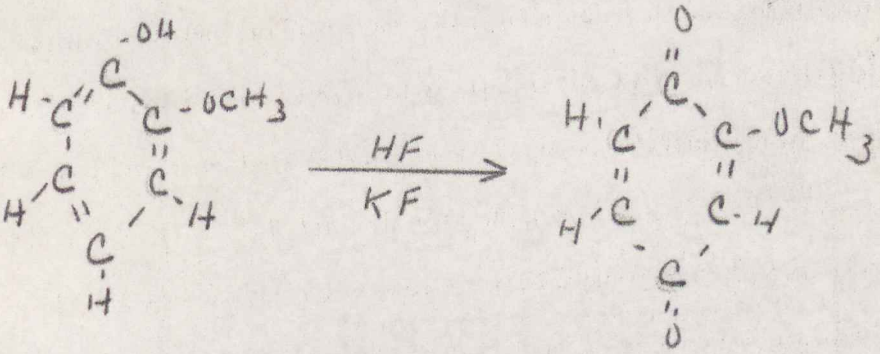
A third reaction was performed. This time the white solid was added to benzene before the ethyl chloride was added. There seemed to be no perceptible reaction.

An attempt was next made to systhesize methoxy-benzoquinone. This could then be used in an analagous determination to see if methoxy-benzoquinone is a product in the reaction of methanol with quinone.

To a solution composed of seven parts of $K_2Cr_2O_7$, fifteen parts of H_2SO_4 and fifty parts of water, are part of guaiacol was added slowly. After the violent reaction had subsided it was allowed to stand for twenty-four hours. The solution was extracted with ether. The extract showed only the presence of some of the original guaiacol. Excess amounts of H_2SO_4 and $K_2Cr_2O_7$ were then used to oxidize the guaiacol.

After standing for a day the mixture was steam distilled. After the distillate was extracted with ether it was found that the only product was again some of the original guaiacol. Tauber and Jellinek had obtained methoxy-benzoquinone from the oxidation of quaiacol by Fremy's salt.(KF and HF).(9) This method was attempted. To .19q. of guaiacol in ether was added one equivalent of an aqueous solution of HF and KF. The solution was shaken for several minutes. Upon extraction with ether the only compound found present was again guaiacol.

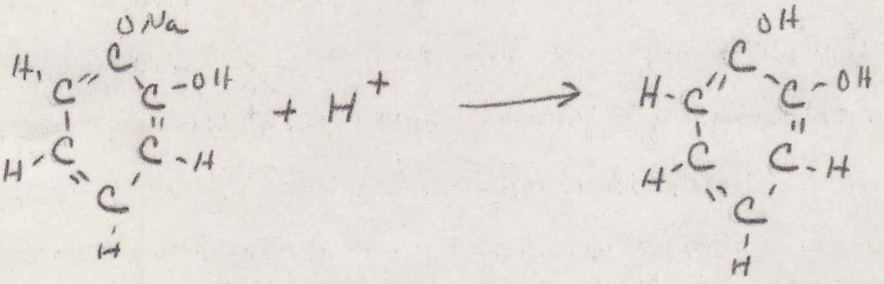




Discussion

As seen, the systhesis of either ethoxy or methoxy benzoquinone was not successful. In the former reaction, the step involving the ethyl chloride seemed to be the trouble spot. When ethyl chloride was added to an alcoholic solution of sodium catecholate there seemed to be no reaction. Acidification and extraction with ether resulted in the original catechol. The probable reason for this is that the ethyl chloride reacted with some of the sodium ethoxide in the alcoholic solution. This would yield ethyl ether.

$$EtCl + EtONa \longrightarrow EtOEt + NaCl$$



To keep this from happening, the sodium catecholate was added to benzene before ethyl chloride was added. This mixture was stirred for several hours. No reaction seemed to have taken place. The ethyl chloride (bp.=7°C.) could not have evaporated since the reaction vessel was tighly stoppered.

In each of the above cases the reactions were run in an atmosphere of nitrogen. If left exposed to the air, the sodium catecholate easily oxidized. This resulted in a black product which could be any combination of oxidation products, including, perhaps, a small amount of ethoxybenzoquinone.

The oxidation of quaiacol with H_2SO_7 and $K_2Cr_2O_7$ to yield methoxy benzoquinone was not successful. The literature source indicated a 20% yield when the oxidation was carried out with o-hydroxy aniline. Since phenols behave essentially like amines in many reactions we expected the same to happen in this case. This apparently is not true. As stated, even a huge excess of oxidizing reagents did not result in any of the desired product. Definite oxidation did take place. The color of the final solution was deep green, indicating that the orange dichromate had been reduced to green Cr^{+++}.

Oxidizing quaiacol by means of Fremy's salt did not produce any results. No reaction took place. From the information given in the literature it can not be seen how this reaction could take place. If H_2SO_4 and $K_2Cr_2O_7$ could not perform the oxidation it can not be seen how HF and KF could. For these two to oxidize without air implies reduction to F and H_2 gas. This is improbable. This reduction might occur in molten HF and KF but not in an aqueous solution.

Summary

A literature source has shown no evidence of the production of ethoxy-benzoquinone from an irradiated solution of quinone in ethanol. Most of the time on this work was thus spent in trying to synthesize this compound. This was not successful. Had this been synthesized, its absorption spectrum could have been obtained. This could have been compared with various separations of the reaction mixture to see if it was indeed a product. The same procedure would have been followed to see if methoxy-benzoquinone is a product in the reaction of quinone in methanol.

Bibliography

1. Fieser, M. and Fiese, L.: *Advanced Organic Chemistry*. Rheinhold Publishing Corp. New York, ; 1961 (845).
2. Leighton, P.A. and Forbes, R.S.: *Journal of American Chemical Society*. *51*, 3549 (1929).
3. Hartley, W.N. and Leonard, A.L.: *J. Chemical Society*, *95*, 34 (1909).
4. Hartely, W.N. and Little, O.H. : *J. Chemical Society*, *90* 1079 (1911).
5. Heiglich, R. : Unpublished
6. Martin. W.B. : Unpublished
7. Poupe, F. : *Coll. Czech. Chemical Communications*, *12*, 225 (1947).
8. Silber, P. : *Berichte Der Deutschem Chemischen Gesellshaft*, *34*, 1531 (1901).
9. Teuber, H.J. and Jellinek, G. : *Berichte Der Deutschen Chemischen Gesellschaft*, *85*, 95 (1952).
10. Wheland, : *Advances in Organic Chemistry*, Wiley and Sons Publishing Corp. New York: 1958 (179).