[Contribution from the Department of Chemistry, Yale University]

THE OXIDATION OF HYDROQUINONE IN THE PRESENCE OF ALIPHATIC AMINES. FORMATION OF BIS(ALKYLAMINO) QUINONES

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During a study of the possibilities of condensing hydroquinone with certain aliphatic amines to form alkyl derivatives of *p*-aminophenol the writer observed that when an aqueous solution of hydroquinone and methylamine was allowed to stand exposed to the air it became red and within a few hours deposited a quantity of brilliant red crystals.[3] Since the reaction appeared to take place first at the surface of the liquid it seemed probable that an oxidation was involved. A solution of hydroquinone and aqueous methylamine was then introduced into a glass tube, after which the air in the tube was displaced by hydrogen and the tube sealed. Another such solution was placed in a second tube which was connected with a bottle filled with oxygen. The contents of the sealed tube remained practically unchanged for months, while the solution which was exposed to oxygen rapidly absorbed the gas, turning pink and then dark and depositing a quantity of the red crystals mentioned above. These red crystals melted at 270° and upon analysis gave values which corresponded to the formula $(C_4H_5ON)_n$. When the compound was boiled with alkali, methylamine was evolved and a quantitative experiment showed that the amount of amine evolved would account for practically all of the nitrogen in the compound (96%). A molecular-weight determination showed that the compound was $C_8H_{10}O_2N_2$. Since the chemical literature appeared to describe no compound of corresponding formula and properties a similar experiment was carried out with dimethylamine and hydroquinone. This yielded a product consisting of dark red needles melting at 171° whose analysis and molecular weight corresponded to $C_{10}H_{14}O_2N_2$. When boiled with alkali, dimethylamine was evolved, the quantity of amine thus obtained accounting for 97% of the nitrogen in the compound. A compound of identical formula whose properties corresponded to this product was prepared by Mylius[4] in 1885 by the interaction of quinone and dimethylamine, which was later shown by Kehrmann[5] to be the tetramethyl deriva-

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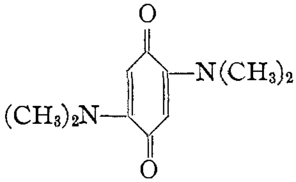
[3] A preliminary paper appeared in *Proc. Nat. Acad. Sci.*, **8**, 57 (1922).

[4] Mylius, *Ber.*, **18**, 467 (1885).

[5] Kehrmann, *Ber.*, **23**, 906 (1890).

tive of 2,5-diaminoquinone:



The experiment of Mylius was then repeated and the two products were found to be identical. (Mylius gives 174° as the melting point while our results showed that both compounds melt at 171°, corr.)

The compound from the oxidation of dimethylamine and hydroquinone is therefore *bis*(dimethylamino)quinone, and this oxidation of dimethylamine-hydroquinone is thus a new method for its synthesis. The red crystals melting at 270°, from the oxidation of methylamine and hydroquinone, must then be *bis*(methylamino)quinone. Further experiments showed that the method of synthesizing these compounds, by the oxidation of the amine and hydroquinone, is a considerable improvement over the method of Mylius. The latter method gives only an insignificant yield of the compound and the product is contaminated with a large amount of humin-like material.[4] On the other hand, by the oxidation of hydroquinone and amine described above a very much higher yield of the compound is obtained and the crystals so formed are practically pure. Hydroquinone, too, is usually a more accessible material than quinone.

Since the compound of Mylius is the only known representative of a *bis*(alkylamino) derivative of benzoquinone [a few *bis*(alkylamino) derivatives of substituted benzoquinones have been prepared, for which see the next paragraph], it was decided to try the oxidation of hydroquinone in the presence of other aliphatic amines, in the hope that analogous *bis*-(alkylamino)-quinones would result. Experiments were carried out upon the oxidation of hydroquinone in the presence of ethylamine, *iso*butylamine, amylamine, allylamine and benzylamine. Alcohol was used as the solvent since a previous experiment with methylamine had shown that it permitted a much better yield than when water was used as a solvent. All of these amines gave the corresponding *bis*(alkylamino)quinone. The resulting products appeared as brilliant red crystals which were practically pure, in some cases so pure that recrystallization was unnecessary. The yields were from 25 to 50%. Secondary butylamine, treated in the same way, also gave crystals of the diamino-quinone but the yield was very low, due perhaps to the use of alcohol as a solvent, in which it is very soluble. With diethylamine oxidation took place but no crystals were deposited and thus far the writer has been unable to isolate any product from the resulting solution.

Since the observation by A. W. Hofmann in 1863 that aniline and quinone will react forming dianilino-quinone and hydroquinone[6] many investi-

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[6] Hofmann, *Proc. Roy. Soc.* (London), **13**, 4 (1863).

gators have prepared aromatic amino-quinones, until at present more than one hundred anilino-quinones are described in the literature.[7] In the aliphatic series, however, only a few amino-quinones are known. Four of these, the diamino-quinones of 2-chloro-5-ethoxyquinone[8] with methylamine and dimethylamine, and those of 2,5-dichloroquinone with *iso*-amylamine and di-*iso*-amylamine,[9] were prepared by substituting amino groups for chlorine atoms or ethoxy groups in the corresponding quinone derivatives, hydrogen chloride or alcohol being split off. The remaining ones, the diamino-quinones of benzoquinone with dimethylamine,[4] glycine ethyl ester and alanine ethyl ester;[10] toluquinone with methylamine[11] and glycine ethyl ester;[10] thymoquinone with methylamine[12] and benzylamine;[13] and *sym*-xyloquinone with methylamine[14] and ethylamine,[11] were all prepared by the interaction of the amine and quinone. In most cases the yields were said to be very low. Some difference of opinion exists regarding the mechanism of this reaction between aliphatic amines and quinone, Mylius[4] stating that the oxidizing agent is the oxygen of the air, while Kehrmann, who investigated the problem five years later,[5] says that the reaction is analogous to that between aniline and quinone, two-thirds of the quinone acting as the oxidizing agent. Since this question has a bearing upon the present investigation, we have examined the behavior of quinone and methylamine and find that in the absence of oxygen no amino-quinone is formed, which would support the conclusion of Mylius. In the case of the amino acid esters, however, Fischer[10] showed that hydroquinone was produced so that these behave toward quinone like the aromatic amines and not like the ordinary aliphatic amines.

That the oxidation of hydroquinone and an aliphatic amine will readily yield the diamino-quinone is perhaps foreshadowed by the observation of Plimpton[15] that in the naphthalene series a *mono*-amino-quinone may result from the oxidation of the amine and naphthoquinol, and also by the statements of Hebebrand[16] and Morner[17] that hydroquinone and certain anilines are very slowly oxidized by the air, giving a minute yield

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[7] For recent extensive studies of anilino quinones and a partial review of the earlier literature see the papers of Suida and his students [*Ann.*, **416**, 113 (1918); *J. prakt. Chem.*, [2] **90**, 467 (1914); *ibid.*, [2] **101**, 268 (1921)].

[8] Kehrmann, *J. prakt. Chem.*, [2] **43**, 260 (1891).

[9] Jackson and Torrey, *Am. Chem. J.*, **20**, 395 (1898).

[10] E. Fischer and H. Schrader, *Ber.*, **43**, 525 (1910).

[11] Fichter, *Ann.*, **361**, 363 (1908).

[12] Zincke, *Ber.*, **14**, 92 (1881).

[13] Wakeman and Groffmann, *Science*, **53**, 218 (1921).

[14] Fichter and Willmann, *Ber.*, **37**, 2384 (1904).

[15] Plimpton, *J. Chem. Soc.*, **37**, 633 (1880).

[16] Hebebrand, *Ber.*, **15**, 1973 (1882).

[17] Morner, *Z. physiol. Chem.*, **69**, 329 (1910).

of the dianilino-quinone. Moreover, Lachowicz[18,19] found that dipiperidyl-quinone results from the atmospheric oxidation of piperidine and hydroquinone.

In regard to the speed of oxygen absorption, by far the most sluggish reaction was with benzylamine—0.25 equivalent in 24 hours—while ammonia, which was tried for comparison with the aliphatic amines, caused the most rapid consumption of oxygen, six equivalents in 24 hours. The other amines are ranged between these two, the speed of oxidation being generally in inverse ratio to the molecular weight.

The production of a *bis*(alkylamino)quinone by the oxidation of an amine and hydroquinone calls for the removal of six atoms of hydrogen and therefore for the consumption of six equivalents of oxygen: $C_6H_4(OH)_2 + 2RNH_2 + 6\left(\frac{O}{2}\right) = C_6H_4O_2(NHR)_2 + 3H_2O$. In all of the cases studied the consumption of oxygen was much greater than six equivalents, while at the same time the yield of *bis*(alkylamino)quinone never approached quantitative figures. With the possible exceptions of dimethylamine and secondary butylamine it seems quite certain that the diamino-quinone formed was practically all precipitated because of its small solubility in the solution used. This can only mean that there has occurred here some other type of oxidation than that required for the production of *bis*(alkylamino)-quinone. The ratio of this excess oxygen to the hydroquinone not used in the formation of *bis*(alkylamino)quinone furnishes an important clue regarding the side reactions. In all cases the oxygen equivalent of this *residual hydroquinone* is considerably higher than six and in some cases it was more than twice this number, namely about 14 for ethylamine. Manchot[20] found that a dilute solution of hydroquinone in alkali is oxidized to quinone with the production of hydrogen peroxide. He also states that several other organic compounds which absorb oxygen have their hydrogen atoms removed, not as water, but as hydrogen peroxide. This suggests that the high oxygen absorption observed in our experiments may be due to the production of hydrogen peroxide. If this were true the formation of a *bis*(alkylamino)quinone would call for the consumption of *twelve* instead of *six* equivalents of oxygen, which would very nearly account for the volume of oxygen actually absorbed. Under the conditions employed this would result in a concentration of 7 or 8% of hydrogen peroxide at the close of the experiment. However, when these solutions were tested, no hydrogen peroxide could be detected, even though one of

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[18] Lachowicz, *Monatsh.*, 9, 505 (1888).

[19] Lachowicz[18] also tried the atmospheric oxidation of hydroquinone in the presence of diethylamine, dipropylamine and diamylamine but obtained only dark resins. Had he used primary aliphatic amines his efforts would no doubt have led to crystalline compounds.

[20] Manchot, *Ann.*, **314**, 177 (1900).

the methods employed would have shown the presence of less than 0.1%. Moreover, it was found that hydrogen peroxide is itself capable of producing the oxidation of hydroquinone-amine to *bis*(alkylamino)quinone in which it is used up. Neither was the large consumption of oxygen due to an oxidation of alcohol or the amine alone, or to a further oxidation of the *bis*(alkylamino)quinone, because a mixture of the aminoquinone and alcoholic methylamine did not absorb oxygen. It is apparently due, then, to a side reaction involving the hydroquinone not converted into the *bis*(alkylamino)quinone. The production of dihydroxy-*bis*(alkylamino)-quinone[21] or a tetra-amino-quinone would call for the consumption of but ten equivalents of oxygen.

In regard to the mechanism of the reaction resulting in the production of *bis*(alkylamino)quinone from oxygen, amine and hydroquinone, our experiments to date do not furnish conclusive evidence. It seems possible that the first step is the formation of a double compound of amine and hydroquinone. Thus, in certain cases, where the amine and hydroquinone were brought together in strong solution the double compound crystallized, and in most of the experiments recorded the hydroquinone was probably first present in large part as an addition product with the amine. Also such double compounds were found to be readily oxidized to *bis*(alkylamino)quinones. On the other hand, we should remember that these double compounds readily dissociate into their components, so they may not be involved in the oxidation. That quinone itself may not be a stage in the reaction is indicated by the low yield secured when quinone was employed as the starting material, but in the experiment reported the concentration of quinone used was much greater than it would be if it formed but a temporary stage in the oxidation.

The great difference between the melting points and other properties of the *bis*(alkylamino)quinones made from closely related amines suggests that this oxidation might be used as a means of identifying certain amines. From our results with impure dimethylamine, it would seem that a slight amount of monomethylamine existing as an impurity in dimethylamine could easily be detected by the oxidation in the presence of hydroquinone, since the *bis*(monomethylamino)quinone is at first the only product and can, moreover, be easily separated from *bis*(dimethylamino)quinone. We might add that tertiary amines probably give no aminoquinones.

The production of isocyanide in some of the oxidation mixtures is also of interest and is supported by Niemeyer's observation[22] that a double compound of aniline and dichloroquinone, when dissolved in alcohol, developed an odor of isocyanide. It was first thought that the presence

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[21] Pinnow [*J. prakt. Chem.*, [2] **98**, 81 (1918)] showed that when hydroquinone is boiled with Fehling's solution it is oxidized to dihydroxyquinone, $C_6H_2O_2(OH)_2$.

[22] Niemeyer, *Ann.*, **228**, 322 (1885).

of alcohol might have something to do with this phenomenon, but a later experiment with only allylamine and hydroquinone still resulted in the same pronounced odor of isonitrile when the mixture was exposed to the action of oxygen.

Experimental Part

Bis(methylamino)quinone, $C_6H_2O_2(NHCH_3)_2$.—Twenty-five g. of hydroquinone was placed in a 500cc. bottle, the air in which was then replaced by oxygen, the bottle connected with an oxygen reservoir, and 200 cc. of 6 *N* aqueous methylamine solution introduced into the bottle. The hydroquinone dissolved with a mild evolution of heat and the bottle was shaken to hasten the solution. At first the resulting solution was practically clear, but almost at once the surface turned red and this color soon spread through the entire liquid. Within ten minutes red crystals were observed on the walls of the bottle where there was a thin film of the solution and within an hour brilliant red crystals were evident throughout the liquid, soon forming a layer on the bottom. During the experiment the oxygen was furnished at practically atmospheric pressure. The total oxygen absorption at various intervals was as follows: 2 hours, 1300 cc.; 5 hours, 2600 cc.; 27 hours, 6000 cc. At this point the solid formed, 3.6 g., was filtered off and the filtrate replaced for further oxidation. Oxygen absorption had practically ceased at the end of 96 hours, with a total oxygen consumption of 13,400 cc. The total weight of product was 5.14 g., or a yield of 14% on the basis of the total hydroquinone used. The material was found to be practically all *bis*(methylamino)quinone. This red product was recrystallized from hot water, alcohol or glacial acetic acid, forming red plates which melted at 270°, corr. At 25° one part of the compound dissolves in 70 parts of glacial acetic acid, 1700 parts of alcohol and 9000 parts of water; while when these solvents are heated to their boiling points one part of the red substance dissolves in about 10 parts of glacial acetic acid, 200 parts of alcohol and 600 parts of water. It is slightly soluble in chloroform and benzene, very soluble in phenol and practically insoluble in ether, gasoline, carbon tetrachloride or carbon disulfide. When boiled with tin and hydrochloric acid it was easily reduced to a colorless solution. The tin was removed with hydrogen sulfide and the latter driven off by boiling. Upon neutralizing the clear acid solution with sodium carbonate there were formed colorless glistening plates which in two or three minutes were oxidized by the air to the original red compound, *bis*-(methylamino)quinone. This re-oxidation to the aminoquinone was also observed when the acid solution of the reduced substance was allowed to stand exposed to the air for several days.

Anal. Calc. for $C_8H_{10}O_2N_2$: C, 57.83; H, 6.02; N, 16.86. Found: C, 57.74; H, 6.18; N, 16.91 (Kjeldahl), 17.05 (Dumas).

Mol. wt. This was found by the ebullioscopic method using glacial acetic acid as the solvent. Calc. for $C_8H_{10}O_2N_2$: mol. wt., 166. Found: 158, 164, 170; av., 164.

A sample of the compound was boiled in a Kjeldahl flask with 200 cc. of water and 30 cc. of 9 *N* sodium hydroxide solution. The evolved vapors were passed through a condenser and then into standard acid in the same manner as with a Kjeldahl analysis after the digestion. The sample, 0.2312 g., evolved by this method a volatile base which neutralized 26.9 cc. of 0.0986 *N* acid. Assuming that the volatile base was ammonia or an amine, this figure would account for 96% of the nitrogen in the compound. The distillate from this process, first neutralized with the standard hydrochloric acid to determine the quantity of the base, was evaporated to dryness and deposited white crystals which were insoluble in chloroform but which dissolved readily in a little hot absolute alcohol. The crystals also gave a positive isonitrile reaction. The volatile base must therefore have been methylamine.

Since by the above reaction the yield of *bis*(methylamino)quinone was low, a second experiment was tried using absolute alcohol as the solvent. This time the reaction was conducted on a smaller scale using 4 g. of hydroquinone and 30 cc. of 9 *N* monomethylamine in absolute alcohol. During the first 24 hours there was absorbed 330 cc. of oxygen with the production of 1.02 g. of the red crystals. At the end of six days the corresponding values were 1380 cc. of oxygen and 2.7 g. of the product, while at the end of 17 days the reaction had practically ceased with a total oxygen consumption of 2030 cc. and a total yield of 3.19 g. of the *bis*(methylamino)quinone. It will be observed that while the speed of the reaction in the alcohol solution was considerably less than in water, and the total oxygen absorbed slightly lower—9.2 instead of 9.8 equivalents of oxygen per mole of hydroquinone used—the yield of aminoquinone was much improved—53% instead of 14%. The oxygen equivalent of the *residual hydroquinone* (hydroquinone not represented by the aminoquinone formed) was 12.8. The dark filtrate from the reaction was tested for the presence of hydrogen peroxide by means of chromic acid and ether, with manganese dioxide, and by titanium sulfate, but in all cases the results were negative. In order to carry out the last test properly, it was necessary to dilute the solution with water until a light pink color was obtained, which rendered the test somewhat less delicate than if it could have been carried out upon the undiluted solution. However, experiments showed that the test was still sufficiently sensitive to easily detect 0.1% of added hydrogen peroxide in the original solution. Therefore, if any peroxide were present the amount must have been very slight. The above filtrate was concentrated upon the steam-bath to about one-third of its original volume. The resulting solution, upon cooling, deposited a quantity of dark yellow crystals which were found to be very soluble in ether. The quantity of the yellow product was not sufficient to establish its identity and it is hoped to obtain shortly a larger amount.

Bis(dimethylamino)quinone, $C_6H_2O_2[N(CH_3)_2]_2$.—Using the smaller oxidation apparatus, there were placed in the reaction bottle 4 g. of hydroquinone and 32 cc. of 5.5 *N* aqueous dimethylamine solution. The dimethylamine had been prepared by the method of Norris and Laws.[23] This solution was oxidized for nine days, consuming 1500 cc. of oxygen and producing 1.5 g. of red needles melting at 171°, corr. This melting point was unchanged when the compound was recrystallized from alcohol or benzene.

Anal. Calc. for $C_{10}H_{14}O_2N_2$: C, 61.85; H, 7.22; N, 14.48. Found: C, 61.84; H, 7.32; N, 14.15 (Kjeldahl).

Mol. wt. This was determined by the cryoscopic method, using benzene as the solvent. Calc. for $C_{10}H_{14}O_2N_2$: mol. wt., 194. Found: 207, 183, 183; av., 191.

When the compound was hydrolyzed with alkali there was evolved a volatile base which was absorbed in standard acid. From 0.2408 g. of the compound the volatile base formed neutralized 24.26 cc. of 0.0986 *N* hydrochloric acid, which would account for 97% of the nitrogen in the compound. The neutralized distillate was soluble in chloroform.

Bis(dimethylamino)quinone was then prepared by the method of Mylius.[4] A mixture made with the red compound prepared by the oxidation of hydroquinone and dimethylamine described above melted at 171° (corr.), as did also the two products tested separately.

Oxidation of Hydroquinone and Dimethylamine Containing a Small Amount of Monomethylamine.—The dimethylamine used in this experiment was prepared by the method of Werner[24] and the experiment was begun with the assumption that we were dealing with pure dimethylamine. However, it was soon evident that monomethylamine

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[23] Norris and Laws, *Am. Chem. J.*, **20**, 51 (1898).

[24] Werner, *J. Chem. Soc.*, **111**, 844 (1917).

was also present and the experiment is given to illustrate the course of the reaction when two amines are present, and also because it suggests a possible method for detecting methylamine as an impurity in dimethylamine. Twenty-five g. of hydroquinone and 200 cc. of 6.5 N aqueous amine were oxidized as in the previous experiment. At the end of six days there had been absorbed 4.7 liters of oxygen and the crystals produced weighed 7.5 g. These crystals were boiled with 100 cc. of absolute alcohol and the portion insoluble in the alcohol weighed 6.1 g. and exhibited all of the properties of *bis*(methylamino)quinone. Since one part of *bis*(dimethylamino)quinone dissolves in ten parts of boiling alcohol it is quite evident that all of it was removed. When we correct for the solubility of the monomethyl compound in boiling alcohol this represents a yield of 6.6 g. of the *bis*(methylamino)quinone. The oxidation of the filtrate was continued and at the end of 15 days the total absorption of oxygen had reached 9 liters and an additional quantity of crystals (5 g.) had been formed. The last crop contained about 0.5 g. of *bis*(methylamino)quinone, the remainder being *bis*(dimethylamino)quinone.

The dimethylamine solution which had been used was then found to give a positive isonitrile reaction and its content of methylamine was estimated as follows. One cc. of the solution was pipetted out and neutralized with dil. hydrochloric acid. This was now evaporated to dryness and the resulting crystals dried overnight in a desiccator. In the morning the crystals were boiled with three portions of chloroform. The chloroform extracts were combined and evaporated to dryness. The portion insoluble in chloroform was titrated against 0.1 N silver nitrate solution and required 6.6 cc. The portion soluble in chloroform was also titrated against the standard silver solution and required 66.1 cc. The molar fraction of the *mono*-amine present was therefore $6.6/(66.1 + 6.6) = 9.1\%$. Had all of the monomethylamine in the solution been converted into *bis*(methylamino)quinone there would have resulted 9.7 g. instead of about 7 g. actually produced.

Bis(ethylamino)quinone.—This was prepared by the oxidation of 13 cc. (9 g.) of ethylamine and 5 g. of hydroquinone dissolved in 15 cc. of absolute alcohol. Within 15 minutes after the material had been introduced into the bottle, crystals had appeared and inside of an hour the bottom was well covered with the substance. The oxygen consumption was as follows: 24 hours, 650 cc.; three days, 1800 cc.; six days, 2200 cc.; 17 days, 2720 cc. At the end of three days the red crystals were removed and weighed 3.35 g. In fourteen more days a further crop of 1.1 g. was produced making a total of 4.45 g. of the *bis*(ethylamino)quinone, or a yield of 50%. This would require 816 cc. of oxygen which would leave 1904 cc. or *fourteen equivalents* of oxygen for the *residual hydroquinone*. The *bis*(ethylamino)quinone melted at 212°. It crystallizes in beautiful red plates. The compound dissolves freely in glacial acetic acid and alcohol, sparingly in ethyl acetate and hot water, and very slightly in cold water, ether and toluene.

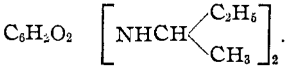
Anal. Calc. for $C_{10}H_{14}O_2N_2$: C, 61.85; H, 7.22; N, 14.48. Found: C, 61.72; H, 7.49; N (Kjeldahl) 13.91, 13.90.

Bis(ethylamino)quinone was also produced when an alcoholic solution of the double compound of hydroquinone and ethylamine, $C_6H_4(OH)_2.C_2H_5NH_2$, was allowed to stand exposed to the air. In this case the yield was not determined but a small amount of the solution yielded a very appreciable crop of the crystals.

Bis(isobutylamino)quinone, $C_6H_2O_2[NHCH_2CH(CH_3)_2]_2$.—In this experiment the oxidizing chamber was a specimen tube and the oxygen holder a 100cc. graduate. In the tube were placed 0.3 g. of hydroquinone, 1 cc. (0.73 g.) of *iso*butylamine and 2 cc. of absolute alcohol. The oxygen consumption was as follows: 3 hours, 18 cc.; 45 hours, 79 cc. The product weighed 0.2 g. and consisted of brilliant red plates, of a slightly lighter color than the corresponding ethyl compound. It was recrystallized from alcohol and melted at 196°. The compound was practically insoluble in hot or cold water, slightly soluble in ether, fairly soluble in alcohol and very soluble in glacial acetic acid.

It was observed that during the course of the oxidation the solution developed a pronounced odor of isocyanide.

Anal. Calc. for $C_{14}H_{22}O_2N_2$: N, 11.20. Found (Kjeldahl): 11.09.

Bis(secondary-butylamino)quinone,  $C_6H_2O_2\left[NHCH\begin{matrix}C_2H_5\\CH_3\end{matrix}\right]_2$.—Five g. of hydroquinone was dissolved in a solution consisting of 10 cc. (7.2 g.) of secondary butylamine and 20 cc. of absolute alcohol. This solution was oxidized with oxygen gas as in the previous experiments. The oxidation was allowed to proceed for 14 days. The volume of oxygen consumed was 1200 cc. The crystals from the reaction weighed 0.7 g. and consisted of long, dark needles melting at 160°. The compound was soluble in alcohol, glacial acetic acid and hot toluene, slightly soluble in ether and ethyl acetate and insoluble in hot or cold water. The solubility in water was so slight that the compound is not attacked by boiling with aqueous alkali.

Anal. Calc. for $C_{14}H_{22}O_2N_2$: N, 11.20. Found (Kjeldahl): 11.06.

Bis(amylamino)quinone, $C_6H_2O_2(NHCH_2CH_2CH_2CH_2CH_3)_2$.—Five g. of hydroquinone and 10 cc. (8.7 g.) of amylamine were dissolved in 20 cc. of absolute alcohol and the solution was exposed to the action of oxygen as in the preceding experiments. The oxidation proceeded with moderate speed, 300 cc. being absorbed in 24 hours and 900 cc. in eight days. Within 24 hours the surface of the solution was almost frozen over by the crystals formed. These were broken loose by shaking and at the end of the experiment the liquid was about half filled with the crystals. The product, weighing 3.3 g., was filtered off and washed with alcohol and then with ether. It consisted of large, flat, purple crystals which were perhaps the most brilliant of the various aminoquinones prepared in this study. They were found to be pure so that recrystallization was unnecessary. Their melting point was 170°. The compound was found to possess about the same solubilities in the various solvents as does the corresponding compound from *iso*-butylamine. The filtrate from this reaction, upon evaporation, deposited a quantity of dark brown crystals which were insoluble in water, soluble in alcohol and very soluble in ether.

Anal. Calc. for $C_{16}H_{26}O_2N_2$: N, 10.06. Found (Kjeldahl): 9.96, 10.00.

Bis(allylamino)quinone, $C_6H_4O_2(NHCH_2CH{=}CH_2)_2$.—Three g. of hydroquinone and 7.5 cc. (5.8 g.) of allylamine were dissolved in 25 cc. of absolute alcohol and the resulting solution exposed to oxygen, as usual. The oxidation proceeded somewhat slowly at first, 300 cc. being consumed in 28 hours, but the total number of equivalents absorbed, 9.8 equivalents (1620 cc.) in 16 days, is almost as high as in any of the other experiments. As the reaction proceeded the solution developed a strong odor of isocyanide. Even when allylamine and hydroquinone were placed together in a tube without the addition of any solvent, oxidation took place forming red crystals and the contents of the tube developed the odor of isocyanide. Another peculiarity of this reaction was that the solution upon oxidation soon developed a green fluorescence. The solid product from the oxidation, 1.97 g. at the end of four days, consisted of brilliant red crystals which after recrystallization from alcohol melted at 195°. This represents a yield of 30%, but the reaction had probably not gone to completion, since the filtrate upon standing exposed to the air deposited more of the red compound.

Anal. Calc. for $C_{12}H_{14}O_2N_2$: N, 12.55. Found (Kjeldahl): 12.36, 12.41.

Bis(benzylamino)quinone, $C_6H_2O_2(NHCH_2C_6H_5)_2$.—When hydroquinone (4 g.) and benzylamine (10 g.) in alcohol (20 cc.) were exposed to the action of oxygen the liquid remained practically colorless for several hours. At the end of 24 hours 50 cc. of oxygen had been absorbed, the solution had acquired a faint green fluorescence and contained a small amount of microscopic bright red crystals. The product had the appearance of rouge. The quantity of the crystals gradually increased and in three days the total oxygen absorbed had risen to 290 cc., the liquid becoming darker and more pronouncedly fluorescent. At this point the red crystals were removed and found to weigh 1.54 g. The filtrate was replaced and further oxidized for twelve days. The total absorption of oxygen in the 15 days was 1240 cc. and the total weight of product was 5.73 g. or a yield of 45% on the basis of hydroquinone employed. The efficiency of the reaction from the standpoint of the quantity of oxygen consumed is much above that for the cases of the other amines studied. Here 56% of the oxygen absorbed was used to produce the 5.73 g. of *bis*(benzylamino)quinone which resulted. The reaction had not reached completion on the fifteenth day, for the filtrate, upon standing exposed to the air, deposited still more of the red product. The *bis*(benzylamino)quinone was practically insoluble in the ordinary organic solvents, alcohol, ether, benzene, chloroform, etc., as well as in water, but dissolved readily in glacial acetic acid. It melted at 246°.

Anal. Calc. for $C_{20}H_{18}O_2N_2$: N, 8.69. Found (Kjeldahl): 8.45, 8.23.

Oxidation of Hydroquinone in the Presence of Ammonia

In order to obtain some information in regard to the effect of alkyl groups on the oxidation of hydroquinone and aliphatic amines, an experiment was carried out with ammonia using 4 g. of hydroquinone and 30 cc. of 10 *N* aqueous ammonia. The solution turned black almost at once and the absorption of oxygen was very rapid, being 1200 cc. in one day, 1450 cc. in two days and 1820 cc. in eight days. No crystals separated and at the end of eight days the liquid had set to a stiff jelly and the absorption of oxygen had practically ceased.

Oxidation of Hydroquinone in the Presence of Sodium Hydroxide

It appeared of interest to see what would be the effect of alkali upon the course of the oxidation of hydroquinone in the absence of amines. Four g. of hydroquinone was dissolved in 30 cc. of 10 *N* aqueous sodium hydroxide. The solution gradually turned brown. At the end of six days it had absorbed 370 cc. of oxygen, which represented 1.7 equivalents, while after fourteen days of oxidation the absorption had practically ceased with a total consumption of 810 cc. or 3.7 equivalents. Thus both the speed of absorption and the total quantity of oxygen consumed were much less than with the aliphatic amines. At the end of the reaction the solution was found to contain brown needles mixed with a quantity of dark material. The identity of the crystals has not been established.

The Reaction between Quinone and Methylamine

A. In the Absence of Oxygen.—A 50cc. bottle was fitted with a two-hole rubber stopper, one hole of which carried a dropping funnel and the other a glass plug. One g. of quinone was introduced into the bottle, after which the stopper was replaced. Hydrogen was passed through the bottle to sweep out the air and then 10 cc. of absolute alcohol was run in. The contents of the bottle were warmed to about 50° to dissolve the hydroquinone and then 12 cc. of 7.5 *N* monomethylamine in absolute alcohol was slowly introduced. Heat was evolved and the liquid turned first brown and then black. The solution was allowed to stand for ten days but no crystals separated.

B. In an Open Dish Exposed to the Air.—The same quantities of quinone, methylamine and alcohol were used as in A. The solution, after being prepared as in A, was placed in a 100cc. beaker and left exposed to the air. At the end of two days the liquid had all evaporated leaving a coating of dark material over the sides and bottom of the beaker. About 75 cc. of water was added and the beaker warmed. The layer of solid material clinging to the sides and bottom of the beaker partly dissolved so that the rest could be broken loose with a stirring rod. The material was filtered and washed. The brown solid which remained weighed 0.56 g. This was recrystallized from 1000 cc. of water, in which it did not all dissolve, and a crop of red crystals was obtained which weighed 0.16 g. This was still not pure *bis*(methylamino)quinone, for upon treatment with ether it partly dissolved imparting a deep brown color to the ether. The yield was therefore below 10%.

C. **In a Closed Bottle Exposed to Oxygen.**—This was a repetition of A except that the reaction bottle was filled with oxygen and connected with an oxygen reservoir. Oxygen was absorbed rapidly and by the end of four days the absorption had practically ceased. The oxygen consumption was as follows: two days, 300 cc.; three days, 455 cc.; four days, 485 cc.; six days, 490 cc. The walls and bottom of the bottle were covered with a brownish-red layer which was easily loosened by means of a glass rod. The solid was filtered off and washed with water, alcohol and ether. It consisted of brown amorphous-looking material and weighed 0.9 g. It was recrystallized from hot water, in which it was not entirely soluble, and yielded 0.44 g. of red crystals which appeared to be impure *bis*(methylamino)quinone. This was recrystallized from 6 cc. of glacial acetic acid which yielded 0.25 g. of a red product. This was still not pure *bis* (methylamino)quinone, for upon extraction with two 30cc. portions of ether a part dissolved to give a brown solution. The brown extract weighed 0.012 g. and contained nitrogen. It is thus evident that quinone is far inferior to hydroquinone as a starting material for the preparation of *bis*(methylamino)quinone.

Action of Hydrogen Peroxide upon Hydroquinone and Methylamine

One-half g. of hydroquinone was placed in a small bottle. The bottle was then closed and the air replaced with hydrogen. Five cc. of 7.5 *N* methylamine in absolute alcohol was introduced, followed by 10 cc. of 3% hydrogen peroxide in water. The solution rapidly became red and then reddish-brown. At the end of 24 hours a layer of glistening red crystals had settled to the bottom and no hydrogen peroxide could be detected in the solution. The material was filtered and the precipitate washed with alcohol and ether. The crystals weighed 0.095 g. and consisted of practically pure *bis*-(methylamino)quinone. The hydrogen peroxide added was sufficient to furnish 4.4 equivalents of oxygen for the hydroquinone employed. The yield of *bis*(methylamino)-quinone was 13% on the basis of the hydroquinone employed, or 17% from the standpoint of hydrogen peroxide used. We hope to repeat this experiment later, using a stronger solution of hydrogen peroxide.

Action of Oxygen upon Bis(methylamino)quinone and Methylamine.—In a small bottle were placed 0.5 g. of *bis*(methylamino)quinone and 10 cc. of 7.5 *N* methylamine in absolute alcohol. The bottle was filled with oxygen and connected as usual with an oxygen supply. The material stood for six days, being shaken at intervals, but no absorption of oxygen could be detected.

The writer wishes to take this opportunity to express his indebtedness to Professor Treat B. Johnson for much helpful encouragement and advice during the progress of this investigation.

Summary

1. When hydroquinone is dissolved in aqueous or alcoholic solutions or primary or secondary amines the resulting solutions will absorb gaseous

oxygen when placed in contact with air or pure oxygen. This absorption of oxygen is quite rapid, as much as 3.8 equivalents per molecule of hydroquinone used, having been absorbed in 24 hours. The total quantity of oxygen consumed is large, the amount varying from 5.6 to 9.8 equivalents per molecule of hydroquinone.

2. With all the primary amines studied, and with dimethylamine, this oxidation caused the separation of brilliant red crystals, which were found to be *bis*(alkylamino)quinones. The yields of these diaminoquinones varied from 14 to 53% on the basis of the hydroquinone used.

3. Much more oxygen gas was consumed than was required for the formation of the *bis*(alkylamino)quinone which separated, the excess being as high as 14 equivalents per molecule of hydroquinone not used to form the *bis*(alkylamino)quinone. The side reaction consuming this extra oxygen has not been determined, but the results have shown that it is not due to the oxidation of alcohol, to a further oxidation of *bis*(alkylamino)-quinone, or to the accumulation of hydrogen peroxide in the solution.

4. This oxidation of hydroquinone in the presence of aliphatic amines furnishes a new, simple and quite efficient method for the preparation of *bis*(alkylamino)quinones, which compounds as a class have heretofore received little study.

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THE ACTION OF DIAZOMETHANE ON SOME AROMATIC ACYL CHLORIDES

II. SYNTHESIS OF FISETOL

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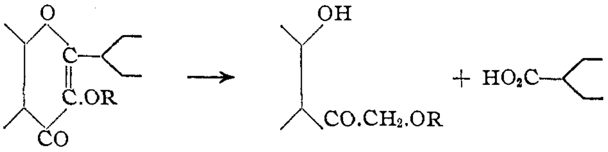
Completely alkylated flavonols (I) are disintegrated by alcoholic potassium hydroxide as follows.



I II III

The production of these disintegration products, especially of those which are derived from Formula II, has served as a basis for the formulas which have been assigned to the following flavonols: fisetin, quercetin, datiscetin, myricetin, quercetagetin and gossypetin. These formulas have been con-