from dil. alcohol; m. p., 315–316° (decomp.). Elbs,[5] who prepared 1,4-dicarboxyanthraquinone by oxidizing 1,4-dimethyl-anthraquinone with nitric acid, states that this acid melts above 300° and that 1,4-dicarboxy-anthracene melts at 320°. Accordingly, the acid was dissolved in ammonia and reduced by the addition of zinc dust. The reduction was known to be complete when the ammoniacal solution became colorless. The zinc dust was filtered off and the filtrate was made acid with dil. sulfuric acid, whereupon a colorless precipitate was obtained. The acid thus obtained was crystallized from dil. alcohol. It melted (with noticeable decomposition) at 320°. This acid was undoubtedly identical with the 1-4-dicarboxy-anthracene of Elbs. Inasmuch as it was prepared from methyl-*iso*propyl-anthraquinone, the relative positions occupied by the methyl and *iso*propyl groups must be the 1 and 4.

Summary

1. 1-Methyl-4-*iso*propyl-anthraquinone has been synthesized from *p*-cymene and phthalic anhydride. The reaction proceeds in two stages: *p*-cymene and phthalic anhydride combine to form cymoyl-benzoic acid; this when condensed in the presence of sulfuric acid yields methyl-*iso*propyl-anthraquinone.

2. Several derivatives of this anthraquinone have been prepared.

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ADDITION COMPOUNDS OF HYDROQUINONE WITH ALIPHATIC AMINES

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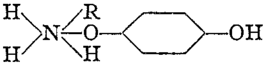
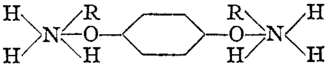
Aromatic amines have been found to form with hydroquinone double compounds[3] which may be formulated as aryl derivatives of mono-ammonium hydroquinone I, or diammonium hydroquinone II,



I



II

So far as the writer has been able to ascertain, the only investigation of the behavior of aliphatic amines with hydroquinone is the work of H. D. Gibbs,[4] in a study of the action of liquid methylamine upon various phenols. At a moderately low temperature hydroquinone was found to combine with

[5] Elbs, *J. prakt. Chem.*, [2] **41**, 1 (1890).

[1] National Research Fellow in Chemistry.

[2] Constructed from a Dissertation presented by Rolla N. Harger to the Faculty of the Graduate School of Yale University in June, 1922, in candidacy for the degree of Doctor of Philosophy. (T. B. Johnson.)

[3] (a) Hebebrand, *Ber.*, **15**, 1973 (1882). (b) Niemeyer, *Ann.*, **228**, 322 (1885); Ger. pat. 174,689, 1906. (c) E. Lumière, A. Lumière and Seyewetz, *Mon. Sci.*, [4] **13**, I, 168 (1899). (d) Dollinger, *Monatsh.*, **31**, 643 (1910). (e) Hock, *Ber.*, **16**, 885 (1883).

[4] Gibbs, THIS JOURNAL, **28**, 1395 (1906).

eight molecules of the methylamine. This compound was unstable at room temperature, evolving methylamine, and leaving behind a white solid which was the diamino compound, $C_6H_4(OH)_2,2CH_3NH_2$. This was stable at room temperature and average barometric pressure but when the pressure was reduced it too decomposed, parting with one-half of its methylamine and leaving behind the mono compound, $C_6H_4(OH)_2.CH_3NH_2$. This last compound formed colorless crystals (m. p., 105°) which in air gradually became red. Although Gibbs made no attempt to determine the cause of the red color, it will be quite obvious from the results reported in the following paper that this was due to its oxidation to *bis*(methylamino)-quinone.

During a study of the oxidation of hydroquinone in the presence of aliphatic amines, described in the following paper, the writer encountered a number of double compounds of hydroquinone with aliphatic amines. These double compounds can be very easily prepared, and since they form perhaps the first step in the process of oxidation of quinol + amine, and also because double compounds of hydroquinone with aliphatic amines are practically unknown in the chemical literature, it was decided to study a few of them. The present short paper deals with the double compounds of hydroquinone with diethylamine, dimethylamine, ethylamine and benzylamine. These compounds exhibit three types of structure: (*a*) a compound of one molecule of hydroquinone with two molecules of the amine, $C_6H_4(OH)_2$, 2HNRR′; (*b*) a compound of one molecule of hydroquinone with one molecule of the amine, $C_6H_4(OH)_2$, HNRR′; and (*c*) a compound consisting of two molecules of hydroquinone joined to one molecule of the amine, $2C_6H_4(OH)_2$, HNRR′ (R = alkyl; R′ = alkyl or hydrogen). While the compounds represented by (*a*) and (*b*) can easily be expressed as alkyl ammonium salts of hydroquinone, according to Formulas I and II, the structure of compound (*c*) is more difficult to picture. So far as the writer knows this last class (*c*) presents an entirely novel type.

Like Hebebrand's[3a] compound of aniline with hydroquinone, these double compounds are not very stable and when they are kept for some time in a closed bottle an odor of the amine can be detected. In the dry state they do not oxidize in the air, but when dissolved in water or alcohol they are rapidly oxidized by atmospheric oxygen. Thus the double compound with ethylamine when dissolved in alcohol formed in one day a fair crop of *bis*(ethylamino)quinone, and the compound with dimethylamine behaved in a similar manner in the presence of a little alcoholic dimethylamine. The aqueous solution of the double compounds is strongly alkaline, suggesting that they are somewhat dissociated under these conditions.

Allylamine, *iso*butylamine, *sec*butylamine, and amylamine, when added to hydroquinone, all caused considerable evolution of heat and upon cooling deposited crystals which are apparently double compounds. Monochloro-hydroquinone and dichloro-hydroquinone appear to form double compounds with aliphatic amines even more readily than does hydroquinone. The time at our disposal has thus far been insufficient to permit the isolation and study of these compounds.

Experimental Part

Addition Compound of Hydroquinone and Diethylamine $[C_6H_4(OH)_2]_2.(C_2H_5)_2NH$.—To a solution of 5 g. of hydroquinone in 100 cc. of ether, was added 10 cc. (6.9 g.) of diethylamine; the molecular ratio (amine: hydroquinone) was 2.1:1. The solution was placed in an ice-bath. After about five minutes crystals began to separate and soon a considerable crop had formed. The crystals consisted of short, thick, transparent prisms which melted at 134°. The weight of product was 4.35 g., corresponding to a yield of 73% on the basis of the hydroquinone used. When the filtrate was concentrated a second crop of crystals was obtained but they were not quite pure. The compound was found to be very soluble in water, alcohol and ether and slightly soluble in benzene and gasoline. When recrystallized from boiling toluene it lost some diethylamine and the resulting product did not melt sharply. The aqueous solution of the compound, when exposed to the air, rapidly turned pink and finally brown. When the compound was dissolved in water or alcohol the solution was strongly alkaline to litmus. In fact it was found that a freshly prepared solution of the compound in water could be titrated with standard acid and the quantity of amine present determined quite as easily as by a Kjeldahl analysis. Ether or benzene solutions of the compound were not oxidized in the air—or at most only very slowly— and the compound in the dry state remained perfectly white for a long time. After two or three months the crystals became slightly brown.

Anal. (Kjeldahl): Calc. for $C_{16}H_{23}O_4N$: N, 4.78. Found: 4.75, 4.81.

Double Compound of Hydroquinone and Dimethylamine, $C_6H_4(OH)_2.(CH_3)_2NH$.—One g. of hydroquinone was dissolved in 30 cc. of absolute ether and the solution cooled in ice. Two cc. (about 1.4 g.) of liquid dimethylamine was then added; the molecular ratio (amine: hydroquinone) was 3.4:1. The flask was stoppered and allowed to stand overnight. In the morning it contained a few transparent crystals of about the size of grains of wheat. As the solution was cooled in a mixture of ice and salt more crystals appeared. The product was filtered off, washed twice with ether and sucked dry. The crystals were placed in a vacuum desiccator for three minutes to remove the last traces of ether, after which they were weighed and analyzed; 0.395 g. was obtained, a yield of 27% on the basis of hydroquinone used. A second crop weighing 0.4 g. was obtained by concentrating the filtrate to about one-half of its original volume and cooling in ice. The second crop was, however, not entirely pure, being too low in its amine content, and upon recrystallization it lost still more of the amine. The first crop of crystals melted sharply at 127°. The compound dissolved readily in water, alcohol and acetone and less readily in benzene and petroleum ether. In ether it was more soluble than the double compound of diethylamine and hydroquinone described in the previous experiment. The compound had an odor of methylamine and upon standing, the crystals, originally transparent, became white at the surface, evidently from the loss of dimethylamine. An aqueous solution was readily oxidized in the air, turning first pink and then dark brown. When the aqueous solution contained methylamine, atmospheric oxidation caused the formation of *bis*(dimethylamino)quinone.

Anal. (Kjeldahl): Calc. for $C_8H_{13}O_2N$: N, 9.03. Found: 8.74.

Double Compound of Hydroquinone with Ethylamine, $C_6H_4(OH)_2.C_2H_5NH_2$.—To a solution of 2 g. of hydroquinone in 50 cc. of dry ether was added 5 cc. (3.3 g.) of ethylamine; the molecular ratio (amine: hydroquinone) was 4.1:1. A clear solution resulted. In about three minutes a white crystalline powder began to appear in clumps and soon the liquid set to a paste. When this was stirred with a glass rod the crystals separated in a layer at the bottom, were filtered off, washed with cold ether and sucked dry. During this stage it was found advisable to blow a stream of illuminating gas on the crystals to prevent the air from coming in contact with them, because while they were still moist with the ether they were rapidly turned bright green by the air. This conversion to the green substance was brought about even more readily by blowing a stream of oxygen upon the crystals while they were still moist with ether. In the dry condition this oxidation did not take place. The crystals were dried in the vacuum desiccator for one hour to remove all the ether and were then analyzed. They melted at 87–90°. When the compound was kept in a stoppered bottle the air above the crystals developed a pronounced odor of ethylamine, so the compound is evidently unstable. This probably accounts for the rather unsharp melting point and for the fact that the nitrogen content was slightly lower than that calculated. The double compound was found to have about the same solubilities in different solvents as did the corresponding double compound of dimethylamine and hydroquinone described in the previous experiment, except that it was much less soluble in ether. When an alcoholic solution of the compound was allowed to stand exposed to the air for 24 hours it was found to contain brilliant red plates. These melted at 190° and their melting point was unchanged when they were mixed with *bis*(ethylamino)quinone, prepared by the oxidation of hydroquinone and ethylamine.

Anal. (Kjeldahl): Calc. for $C_8H_{13}O_2N$: N, 9.03. Found: 8.70, 8.67.

Double Compound of Hydroquinone with Benzylamine, $C_6H_4(OH)_2.[C_6H_5CH_2NH_2]_2$.—In a dry test-tube were placed 7 cc. of anhydrous benzene and 1 g. of hydroquinone, and to this 1.5 cc. (1.5 g.) of benzylamine was added; the molecular ratio (amine: hydroquinone) was 1.5:1. Heat was evolved and the original light needles of hydroquinone were sintered together to a hard mass. The mixture was heated to effect solution and as it cooled crystals were deposited. These were recrystallized by dissolving in boiling ether and then cooling the ether solution to —18° in an ice-salt mixture. This yielded a good crop of long, silky needles; m. p., 71°.

Anal. (Kjeldahl): Calc. for $C_{20}H_{24}O_2N_2$: N, 8.64. Found: 8.52.

Summary

1. Hydroquinone has been found to unite with primary and secondary aliphatic amines, forming crystalline addition compounds.

2. The addition products with diethylamine, dimethylamine, ethylamine and benzylamine have been investigated.

3. The compounds studied present three types: Hq_2Am, HqAm and $HqAm_2$ (where Hq = hydroquinone and Am = amine).

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