tube, in larger quantity equal to that of liquid in the corona tubes. The solid is gummy or resinous, inert toward solvents and chemical reagents except strong oxidizing reagents.

7. In corona discharge a small amount of free carbon is deposited on the metal electrode in tree-like formation.

8. A close correlation of index of refraction, molecular weight, density, color and viscosity characterizes all the liquid products. Increase in all these properties is inversely proportional to the *yield*, for which a simple explanation is given.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIDDLEBURY COLLEGE]

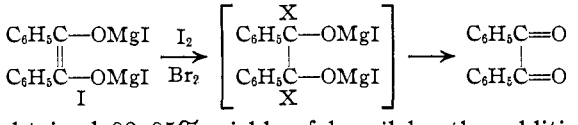
OXIDATION OF BENZOINS TO DIKETONES WITH IODINE

BY BEN B. CORSON AND ROBERT W. McALLISTER

RECEIVED MAY 10, 1929 PUBLISHED SEPTEMBER 5, 1929

Benzoin, anisoin, piperoin, furoin, etc., are easily oxidized to the corresponding diketones by various methods. On the other hand, the conversion of aliphatic analogs of benzoin such as butyroin, $C_3H_7CHOHCO\text{-}C_3H_7$, into diketones is not so convenient. We have studied the oxidizing effect of iodine, thinking that the reaction might be applicable to aliphatic acyloins. Solid aromatic acyloins were used in the investigation since they are easier to manipulate than the liquid aliphatic analogs. Although the reaction seems of no value in the preparation of aliphatic diketones, some of the results which came to light are of general interest.

The reaction is based on a recent observation of Gomberg and Bachmann[1] that benzil results from the action of iodine or bromine on stilbenediolate (I).



We have obtained 90–95% yields of benzil by the addition of iodine to alkaline solutions of benzoin. Benzoin was dissolved in methyl alcohol and sodium methylate was added, followed by iodine. Due to the extreme sensitiveness to oxidation of an alkaline solution of benzoin, the reaction mixture must be protected from air. This was accomplished either by working in an atmosphere of dry nitrogen or by keeping the alcohol solution boiling throughout the duration of the reaction. Similar yields of diketone (80 to 90% of the theoretical amount) were obtained from anisoin, piperoin and furoin.

It seems quite likely that the mechanism of this reaction is that described by Gomberg, namely, the removal of sodium from the dienolic

[1] Gomberg and Bachmann, THIS JOURNAL, 49, 2584 (1927).

salt. However, the interaction of benzoin with sodium methylate does not yield stilbenediolate, as would be required for the above mechanism. According to Meisenheimer,[2] the product is a white salt which contains one atom of sodium per two molecules of benzoin, $C_{28}H_{23}O_4Na$. If our suggested mechanism be correct, this salt must be in equilibrium with disodium stilbenediolate.

$$4\begin{matrix}C_6H_5CHOH\\ |\\ C_6H_5CO\end{matrix} \xrightarrow{2NaOCH_3} 2C_{28}H_{23}O_4Na \rightleftharpoons \begin{matrix}C_6H_5CONa\\ \|\\ C_6H_5CONa\end{matrix} \xrightarrow{I_2} \begin{matrix}C_6H_5CO\\ |\\ C_6H_5CO\end{matrix} + 2NaI$$

A deep reddish-purple color appears immediately when sodium methylate is added to a methyl alcohol solution of benzoin. When a small amount of iodine is added, the color quickly fades to straw yellow, but in a few moments the purple color returns. Also, the admission of a small amount of air discharges the color but the original purple color quickly reappears when air is prevented from entering. Gomberg[1,3] observed a similar behavior with his unsaturated halomagnesium glycolates. He suggests that the remarkable reactivity of the latter may be due to a partial opening of the double bond. These color changes could be explained in the same manner.

$$2C_{28}H_{23}O_4Na \rightleftharpoons \underset{\begin{matrix}|\quad|\\ ONa\ ONa\end{matrix}}{C_6H_5C{=}{=}CC_6H_5} \rightleftharpoons \underset{\begin{matrix}|\quad|\\ ONa\ ONa\end{matrix}}{C_6H_5C{=}{=}CC_6H_5}$$

II III

The color would be due to the free valented form (III); iodine or oxygen momentarily removes it from the equilibrium. Whatever may be the significance of the color of an alkaline solution of benzoin, it nevertheless serves as a delicate test for the latter.

Experimental Part

Oxidation of Benzoin.—At first the oxidation reaction with sodium methylate and iodine was carried out in air but the benzil was always impure. In order to discover what impurities might result due to air, we carried out the following run. Twenty-one grams of benzoin was dissolved in 500 cc. of hot methyl alcohol and 7.5 g. of sodium, dissolved in 100 cc. of methyl alcohol, was added. Considerable light purplish solid separated from the dark solution. The mixture was heated to $\pm 50°$ for half an hour and mechanically stirred while a stream of compressed air was blown into the flask. The solid finally disappeared; the solution was still dark colored at the end of the half hour. We isolated 2 g. of benzil and 12 g. of benzoic acid, which accounts for 60% of the original benzoin. When the oxidation of benzoin with methylate and iodine was run in an atmosphere of dry nitrogen or in boiling methyl alcohol, pure benzil was obtained in 90 to 95% yields. The conditions are described in the preparation of furil. The methyl alcohol must be free from acetone, ethyl alcohol, etc., else iodoform will contaminate the product.

Oxidation of Furoin.—Ten grams of furoin was dissolved in 225 cc. of boiling methyl alcohol and to the boiling solution was added a hot, freshly prepared solution of

[2] Meisenheimer, *Ber.*, **38**, 874 (1905); cf. Garner, *Am. Chem. J.*, **32**, 583 (1904).

[3] *Cf.* Hantzsch and Glower, *Ber.*, **40**, 1519 (1907).

sodium methylate made by dissolving 2.5 g. (105% of the calculated amount, assuming the product to be a disodium derivative of dienol) of sodium in 50 cc. of pure methyl alcohol. To the boiling solution was then added, in three portions, 14 g. (106% of the calculated amount based on sodium) of iodine. The final color of the solution was brown. The heat was then removed; furil immediately began to crystallize. The mixture was allowed to cool to room temperature and filtered. A small additional yield was obtained by concentrating the mother liquor. The total yield of air-dried product, melting point 164–165° (corr.), was 8 g. (80% of the theoretical amount). The best solvent for crystallizing furil is benzene. Pure furil melts at 165 to 165.5° (corr.). When bromine is substituted for iodine, there is a resultant drop in yield of 20 to 30%.

Until recently the only practical preparation of furil was air oxidation of a cold alkaline solution of furoin as described by E. Fischer.[4] Recently a new method has been described by Nisbet[5] which involves the use of nitrobenzene as oxidizing agent.

In the oxidation of benzoin we used twice the amount of sodium methylate required to form stilbenediolate. This seemed to be the best amount. However, when this proportion of sodium was used with furoin, the yield of furil dropped 40%; with furoin the sodium methylate should be barely in excess.

Preparation of Furoin.—Furoin was prepared by Fischer's directions.[4] The purity of the crude product depends greatly upon the quality of the furfuraldehyde. If the latter is very impure, it is almost impossible to obtain pure furoin. We purified the crude product as follows. The crude furoin (dark brown and apt to be sticky) was air-dried and then allowed to stand for twelve hours in ether. It was filtered and then soaked in fresh ether for a second twelve hours, after which it was again filtered by suction. The ether removed a black tar. The furoin was dissolved in boiling ethyl alcohol (≐150 g. per 500 cc. of alcohol) and precipitated by slowly pouring the hot alcohol solution into 5 volumes of water with rapid stirring. The solid was filtered, dissolved in alcohol and precipitated again with water. The process was repeated once more. The final product was of a light tan color and the supernatant aqueous alcohol from which it separated was clear and red. The first precipitation yielded a product which filtered slowly. However, the second and third precipitations gave a product which filtered very nicely. Finally, the furoin was crystallized from hot ethyl alcohol, filtered by suction, washed with ether and air-dried. Pure furoin melts at 138–139° (corr.).

Benzoin Color Test.—The purple color of an alkaline solution of benzoin has long been used as a color test for both benzoin and benzil,[6] but it has never been evaluated quantitatively. Using our procedure a positive color test is given by 0.0002 g. of benzoin and a weak test with 0.0001 g. This is one hundred times or so as sensitive as the test with Fehling's solution. Under the conditions of the test benzil alone gives no purple color even when the solution is warmed. However, benzil added to the test solution intensifies the benzoin color. The intensification is slight but it is unmistakable. This deepening of color would seem to be evidence of quinhydrone formation.[7]

The procedure consists in first adding to a 10-cc. test-tube 1 cc. of sodium methylate solution (4 g. of sodium in 50 cc. of methyl alcohol), next 0.1 cc. of saturated benzil solution and, finally, anywhere from 0.02 to 1 cc. of the methyl alcohol solution of benzoin to be tested.

This color test can be applied to furoin and benzofuroin, the former giving a navy

[4] Fischer, *Ber.*, **13**, 1334 (1880); *Ann.*, **211**, 214 (1882).

[5] Nisbet, *J. Chem. Soc.*, 3121 (1928).

[6] Liebermann and Homeyer, *Ber.*, **12**, 1975 (1879); Bamberger, *ibid.*, **18**, 865 (1885); Scholl, *ibid.*, **32**, 1809 (1899); Hantzsch and Glower, *ibid.*, **40**, 1519 (1907).

[7] Scholl, *ibid.*, **32**, 1809 (1899).

blue with sodium methylate, the latter a delicate amethyst. In both cases the color is deeper in the presence of furil, benzofuril or benzil. On the other hand, neither piperoin nor anisoin give any color with methylate; neither does piperil nor anisil intensify the color of benzoins that do give color, namely, benzoin, furoin and benzofuroin.

Simple sugars are similar to benzoin inasmuch as they have a carbonyl group adjacent to hydroxyl. Levulose, however, does not respond to the color test; neither does butyroin, $C_3H_7CHOHCOC_3H_7$, a typical aliphatic acyloin.

We compared the delicacy of the color test against that of the Fehling test. The smallest amount of benzoin capable of yielding a significant precipitate of cuprous oxide in an hour was 0.01 g. An immediate color change on simple heating required 0.02 g. to 0.05 g. This is a poor test when compared with the color reaction with sodium methylate, which gives an immediate and conclusive purple color with 0.0002 g. of benzoin. The extreme limit of the Fehling test is 0.005 g. of benzoin. At this dilution the mixture must stand for two hours or more and the indication which finally results is very doubtful.

This work was aided by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. Various analogs of benzil can be prepared by iodine oxidation of alkaline solutions of the corresponding benzoins. A mechanism involving stilbenediolate is suggested.

2. The frequently described delicate color test with alcoholic alkali is shown to be applicable to certain benzoins but not to others. It is suggested that the color is indicative of trivalent carbon.

MIDDLEBURY, VERMONT

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 44]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. IX. THE VAPOR PRESSURES, DENSITIES AND REFRACTIVE INDICES OF CERTAIN BINARY MIXTURES

BY SPENCER W. PRENTISS

RECEIVED MAY 13, 1929 PUBLISHED SEPTEMBER 5, 1929

In the seventh paper of this series the velocity constants of the reaction at 25° between pyridine and ethyl iodide in a number of solvents were presented. The relative values of the constants, indicating the adjuvance of the solvents, were as follows.

TABLE I

VELOCITY CONSTANTS

Benzene	1	*n*-Propyl alcohol	1.11
Nitrobenzene	25	*n*-Butyl alcohol	1.11
Acetone	12.8	*Iso*propyl alcohol	1.07
Methyl alcohol	2.5	*Sec.*-butyl alcohol	1.00
Ethyl alcohol	1.4	*Tert.*-butyl alcohol	0.93