

of ferric formate. When 30 cc. of the distillate was neutralized with sodium hydroxide the solution, then made acid to litmus with hydrochloric acid, and a solution of mercuric chloride added and the mixture digested on the water-bath, a white precipitate soon began to form. A large amount of calomel was obtained, covering the entire bottom of the beaker. These results show conclusively that the acid contained in the distillate was formic acid.

The Quantitative Determination of the Pyrimidines.—The solution remaining from the ether extraction was worked for the pyrimidines according to the directions given in one of our previous papers.² After the removal of sulfuric acid with barium hydroxide, and the purines with silver sulfate in acid solution, the pyrimidines were precipitated in the usual manner as silver salts. These salts were decomposed with hydrogen sulfide and the cytosine removed as the phosphotungstate. After decomposition of this salt with barium hydroxide the cytosine was isolated as the base; 0.37 g. was obtained, corresponding to 9.7% of the weight of nucleic acid used.

The filtrate left from the phosphotungstate precipitation was freed from this reagent with barium hydroxide, the barium removed in the usual way and the solution evaporated to dryness. The residue was taken up in water and filtered from a small amount of insoluble material and the solution again evaporated to dryness and weighed. The crude thymine weighed 0.45 g., corresponding to 11.8% of the weight of the nucleic acid used. All of our solutions failed to respond to tests for uracil.

Summary

1. It has been shown that the sugar functioning in tuberculinic acid is a hexose. This was proven by identification of levulinic and formic acids as products of its hydrolysis.

2. A new analysis for pyrimidines in tuberculinic acid has been made and results have been obtained which are identical with those reported in our previous publication.²

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]
THE ACTION OF ULTRAVIOLET LIGHT UPON DIKETONES

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In aqueous solution benzil is converted into benzilic acid by warming it with an alkali. The reaction is rapid and practically quantitative. It has been reported that the same rearrangement occurs slowly in the absence of alkali when benzil, in moist ether, is exposed to sunlight.¹ Under similar treatment benzil in alcohol yields benzoic acid and benzoin.²

This investigation was undertaken to determine the action of radiant energy of short wave lengths upon aqueous and alcoholic solutions of benzil and the corresponding aliphatic diketone, diacetyl.

Preliminary tests were made with saturated aqueous solutions of benzil. The solutions were placed in open beakers with the liquid surfaces 18 cm. below a 110-volt quartz mercury-vapor lamp. Samples were withdrawn

¹ Klinger, *Ber.*, 19, 1868 (1886). Lachman, *THIS JOURNAL*, 44, 330 (1922).

² Ciamician and Silber, *Ber.*, 36, 1575 (1903).

every 3 hours and titrated with sodium hydroxide solution. There was a gradual development of acid but an exposure of at least 30 hours was required to secure enough of the product for identification. Benzoic acid was the principal product.

Because of the slight solubility of benzil in water (0.33 g. per liter at 20°) mixtures of alcohol and water were used in the later experiments, and since ethyl alcohol is oxidized by the oxygen of the air under the influence of the ultraviolet light, blank determinations with the solvent alone were made under the same conditions. The acetic acid which developed in the blank tests (100cc. portions) amounted to approximately 1.2×10^{-6} moles per hour. Within 12 hours the benzil in 66% alcohol was completely converted into other products.³ The solvent was then removed by evaporation. By repeated extractions with hot water we obtained from the yellow tarry residue a mixture of colorless crystals. Approximately 80% of this crystalline part of the product was benzoic acid. The remainder was salicylic acid.

The mechanism for the production of these acids from benzil has been determined. The first step is hydrolysis of the diketone resulting in the production of benzoic acid and benzaldehyde. Atmospheric oxidation of benzaldehyde to benzoic acid is catalyzed by ultraviolet light and salicylic acid is formed from benzoic acid under the same conditions. A qualitative test for salicylic acid can be obtained when an alcoholic solution of benzoic acid is exposed to the ultraviolet light for less than an hour. When air was excluded by making the exposures in quartz flasks in an atmosphere of nitrogen no salicylic acid was formed. Under these conditions the oxidation of benzaldehyde was prevented, also, and the aldehyde appeared as one of the final products. Benzoin was produced in considerable quantities in the oxygen-free samples but we have not yet determined whether the production of benzoin is due entirely to reduction of benzil by alcohol or is due in part to a condensation of benzaldehyde.

In order to determine whether benzilic acid could be an intermediate product we exposed both water and alcohol solutions of pure benzilic acid. The solutions became cloudy in the first half hour of exposure. Two products were isolated. One was benzopinacol, $(C_6H_5)_2 \cdot COH \cdot COH \cdot (C_6H_5)_2$, and the other benzophenone. These products were never obtained from benzil.

Experimental Part

Benzil in Dry Benzene.—Several 50cc. portions of a 1% solution of benzil in dry, oxygen-free benzene were placed in quartz flasks, boiled to

³ The test for benzil was made by boiling the solution with an alkali, evaporating to dryness, and treating the residue with concd. sulfuric acid. Under this treatment, a mere trace of benzil yields benzilic acid in sufficient quantity to impart a red color to the sulfuric acid.

expel air from the solution, and the air of the flasks was replaced by pure nitrogen. Mercury seals were placed about the necks of the flasks. The solutions were exposed for 1 to 7 hours at a distance of 20 cm. from a 220-volt mercury arc. They acquired a light straw color as does pure benzene alone. When the solution was evaporated to dryness the benzil was recovered unchanged.

Benzil Vapor Exposed.—When exposed at a temperature of 200° in an evacuated flask for 6 hours, 0.2755 g. of benzil yielded 18 cc. of carbon monoxide (0°, 760 mm.) and a corresponding quantity of benzophenone. A flask containing benzil protected from the light by tin foil was kept in the same thermostat during the same interval of time. There was no thermal decomposition of the benzil.

Benzil in Water.—Several 50cc. portions of an aqueous solution of benzil (0.3 g. per liter) were exposed in quartz flasks in the presence of air. The increase in acidity during 30 hours is indicated in the following table.

TABLE I
INCREASE IN ACIDITY OF AN AQUEOUS SOLUTION OF BENZIL UPON EXPOSURE
TO ULTRAVIOLET LIGHT

| | | | | | | | | | | |
|-----------------------|------|------|------|------|------|------|------|------|------|------|
| Time, hours..... | 3 | 6 | 9 | 12 | 15 | 18 | 21 | 24 | 27 | 30 |
| 0.062 N NaOH, cc..... | 0.26 | 0.48 | 0.70 | 0.92 | 1.12 | 1.32 | 1.50 | 1.66 | 1.84 | 1.94 |

Benzil in Alcohol and Water.—A stock solution was prepared by dissolving 2 g. of benzil per liter in 66% ethyl alcohol; 100cc. portions of this solution were exposed in quartz flasks. At the same time 100cc. portions of the pure solvent were exposed. At each interval indicated in the following table a benzil solution and a blank were withdrawn and titrated. The amount of the base reported is the difference between the two titrations.

TABLE II
EXPOSURE OF BENZIL IN WATER AND ALCOHOL

| | | | | | | | | | | |
|---------------------|------|------|------|-------|-------|-------|-------|-------|-------|-------|
| Time, hours..... | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 0.062 N NaOH, cc... | 4.28 | 6.30 | 8.70 | 10.72 | 13.35 | 15.40 | 16.50 | 17.20 | 17.82 | 18.06 |

Assuming that 2 mols. of acid are derived from each mol. of benzil, this represents only a little more than 50% conversion, but the benzil had completely disappeared. Approximately half of it was converted into a resinous product, which we have not identified, and half was converted into benzoic acid. Part of the benzoic acid was oxidized to salicylic acid. The crystalline product was usually 80% to 90% benzoic acid and 20% to 10% salicylic acid.

Exposures in the Absence of Air.—Solutions of benzil in aqueous alcohol were exposed to a 220-volt lamp for 8 hours in the absence of air. A white precipitate formed and was identified as benzoin (m. p., 132–134°). Benzoic acid was isolated as in previous cases, but no salicylic acid was produced. The pure solvent (66% alcohol) under nitrogen yielded no acetic acid. Some hydrogen was produced from both the pure solvent

and the benzil solution. This is due to the decomposition of the ethyl alcohol into acetaldehyde and hydrogen.⁴ Alcohol thus acts as a reducing agent producing benzoin from benzil.

Benzilic Acid Exposed.—Benzilic acid, when dissolved in 50% alcohol and exposed to ultraviolet light, is converted into benzopinacol. When air is present benzophenone is produced also; but in the absence of air benzophenone is reduced to benzopinacol so rapidly that it never appears as a final product of the reaction.

Diacetyl in Water.—A stock solution of diacetyl was prepared by dissolving 2 g. of the diketone in 1 liter of water; 100cc. portions of this solution were exposed at a distance of 14 cm. from a 220-volt lamp. The substance was converted into acetic acid and acetaldehyde. The rate of acid formation is indicated by the following measurements.

TABLE III
EXPOSURE OF DIACETYL IN WATER

| | | | | | | | | | | |
|----------------------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Time, hours..... | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 0.01 N NaOH, cc..... | 70 | 100 | 118 | 130 | 138 | 144 | 148 | 151 | 152 | 153 |

Diacetyl Vapor.—A quartz flask having a capacity of 125 cc. was filled with diacetyl vapor at 100° and 1 atmosphere pressure and exposed to ultraviolet light. Gas was evolved at the rate of 8 cc. per minute. The gas was collected over mercury and analyzed. It was found to be carbon monoxide (2 vols.) and ethane (1 vol.).

Summary

Under the influence of ultraviolet light, benzil in the vapor state is decomposed into carbon monoxide and benzophenone when the temperature is 200° or above.

In dil. alcohol, in the absence of air, it is partly hydrolyzed to benzoic acid and benzaldehyde, but a portion of it is reduced by the alcohol to benzoin.

In aqueous alcohol in contact with air it is converted into benzoic acid. Further oxidation of the benzoic acid gives some salicylic acid.

Benzilic acid is not formed in solutions of benzil. The decomposition products of benzilic acid, namely, benzopinacol in the absence of oxygen, and benzophenone and benzopinacol in the presence of oxygen, were never found in the exposed benzil solutions.

Under the influence of ultraviolet light, diacetyl vapor yields ethane and carbon monoxide.

An aqueous solution of diacetyl yields acetic acid and acetaldehyde.

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⁴ Berthelet and Gaudechon, *Compt. rend.*, **153**, 383 (1912).