guinea-pig skin, treated for several hours at 40.00° in trypsin solutions of 0.1 to 0.4%, showed considerable loss of collagen. J. A. Wilson and A. F. Gallun[15] have also shown that calfskin, after a preliminary passive period, may be almost completely hydrolyzed with trypsin. It may be remarked that no such concentrations of trypsin as those herein indicated are obtained in using the ordinary commercial bates in practice.

Summary

A study has been made of the hydrolysis of collagen with trypsin, by controlling the acidity of the pre-treatment and digestion, and examining the effects of varying the time of digestion, concentration of enzyme, and size of collagen particles. The optimum hydrion concentration for the hydrolysis is found to be at P_H 5.9. Pre-treatment of the collagen in solutions of various degrees of acidity does not influence the subsequent tryptic digestion. The speed of hydrolysis increases as the size of the substrate particles diminishes, the action taking place probably at the surface of the particles. Hydrolysis increases with increasing concentration of trypsin, but never reaches completion under the limits of experimental conditions. The reversibility of the reaction is discussed, and the similarity between the action of trypsin on insoluble and soluble substrates is demonstrated.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE BENZIL REARRANGEMENT. III

BY ARTHUR LACHMAN

Received February 10, 1923

In the preceding papers[1] of this series, it has been shown that the conversion of benzil into benzilic acid may be regarded as an addition of water, or of alkali hydroxide, to one of the carbonyl groups, followed by an interchange of one of the hydroxyl groups thus formed with phenyl.

$$C_6H_5—CO—CO—C_6H_5 \longrightarrow C_6H_5—C(OH)_2COC_6H_5 \longrightarrow (C_6H_5)_2C(OH)CO(OH) \quad (1)$$

Intramolecular rearrangement (metakliny) of this sort, which also involves simultaneous oxidation and reduction, is always accompanied, to a greater or less extent, by a rupture of the molecule.

The present paper deals with the action of potassium cyanide on benzil. This interesting reaction was first reported by Jourdan.[2] Jourdan rubbed 20 g. of benzil in a mortar with 10 cc. of alcohol and 1 g. of potassium cyanide. The benzil disappeared completely in a short time; it was converted into a mixture of ethyl benzoate and benzaldehyde.

$$C_6H_5—CO—CO—C_6H_5 + KCN + C_2H_5OH = C_6H_5CHO + C_6H_5CO—OC_2H_5 + KCN \quad (2)$$

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[15] Wilson and Gallun, *J. Ind. Eng. Chem.*, **14,** 834 (1922).

[1] Lachman, THIS JOURNAL, **44,** 336 (1922); **45,** 1509 (1923).

[2] Jourdan, *Ber.*, **16,** 659 (1883).

With water instead of alcohol, he obtained benzaldehyde and benzoic acid. The reaction was much slower in this case.

The Action of Potassium Cyanide on Benzil

Jourdan's work was repeated. The reaction is accompanied by considerable heat, and is completed within a very few minutes—from 2 to 10, depending upon concentration. The ethyl benzoate was always entirely free from benzilic acid.

As the addition of water to benzil and sodium ethoxide produces increasing amounts of benzilic acid, aqueous alcohol was also tried with Jourdan's reaction.

It is possible to estimate a fraction of a milligram of benzilic acid. Not even this small amount could be found when 10 g. of benzil was acted upon by potassium cyanide in 100 cc. of 25% alcohol. This catalyst, then, ruptures benzil without effecting any rearrangement.

The experiment just described also afforded another interesting observation. The benzil was completely ruptured; but in spite of the low alcohol concentration, over 90% of the benzoic acid appeared as ethyl benzoate. The formation of ethyl benzoate under these conditions pointed to benzoyl cyanide as the primary product of the rupture.

$$C_6H_5{-}CO{-}CO{-}C_6H_5 + KCN + H_2O = C_6H_5CO{-}CN + C_6H_5CHO + KOH \quad (3)$$

This then, according to the well-known behavior of acyl halides in presence of alkalies, acts upon the alcohol with the formation of ethyl benzoate and potassium cyanide.

$$C_6H_5{-}CO{-}CN + C_2H_5OH + KOH = C_6H_5CO{-}OC_2H_5 + KCN + H_2O \quad (4)$$

The latter salt enters the cycle again.

It was possible to show, first, that benzoyl cyanide acts almost instantly on weakly alkaline alcohol; and second, that it is actually formed when anhydrous hydrocyanic acid is allowed to act upon benzil.

The Action of Hydrocyanic Acid on Benzil

The action of hydrocyanic acid on benzil, in alcohol solution, was studied by Michael and Palmer.[3] They dissolved benzil in alcohol, added rather large proportions of potassium cyanide, *heated until all was dissolved*, and then added hydrochloric acid. They obtained ethyl benzoate and benzaldehyde, and attributed the result to "nascent hydrocyanic acid," because that acid, in the "free" state, did not act upon benzil below 200°. It is clear that in Michael and Palmer's experiment benzil was ruptured before "nascent" hydrocyanic acid was produced. Moreover, benzil is in fact ruptured[4] by hydrocyanic acid and alcohol at temperatures below 100°. The only difference between the action of potassium cyanide on benzil and that of hydrocyanic acid lies in the much greater velocity of the former.

[3] Michael and Palmer, *Am. Chem. J.*, **7**, 190 (1885).

[4] Compare also Michael, THIS JOURNAL, **42**, 814 (1920).

Benzilo-dicyanohydrin

Benzil directly adds two molecules of hydrocyanic acid, to form benzilo-dicyanohydrin.[5] This substance is best prepared by heating benzil with anhydrous hydrocyanic acid to 90–95°; the yield is almost quantitative.

Some of the recorded data concerning benzilo-dicyanohydrin need correction. Zinin states that it is stable towards boiling water; on the contrary, it is quantitatively dissociated into benzil and hydrocyanic acid in a short time. Zinin further reported a reaction which seemed to have significance for the present investigation, namely, the formation of ethyl benzoate when benzilo-dicyanohydrin is boiled with alcohol and mercuric oxide, with reduction of the latter to metallic mercury. This reaction does not take place; the reaction products are benzil and mercuric cyanide; mercuric oxide dissociates the cyanohydrin, but does not oxidize it.[6] Benzilo-dicyanohydrin is a true nitrile, and produces diphenyl-tartaric acid[5b] when hydrolyzed.

$$C_6H_5{-}C(OH)\,(CN){-}C(OH)\,(CN)C_6H_5 + 4\,H_2O{=}C_6H_5{-}C(OH)(COOH){-}C(OH)\text{-}(COOH)C_6H_5 + 2\,NH_3 \quad (5)$$

This structure also accounts for a new and curious reaction which takes place when the dicyanohydrin is dissociated by heat, under pressure. It was expected that this dissociation would yield benzoyl cyanide and mandelonitrile.

$$C_6H_5{-}C(OH)(CN){-}C(OH)(CN)C_6H_5{=}C_6H_5{-}CO{-}CN + C_6H_5{-}CH(OH){-}CN \quad (6)$$

Instead, the chief product was a high-boiling oil which slowly crystallized. It melted at 61°, and had the composition of the unknown benzilo-monocyanohydrin. Its properties, however, pointed to the benzoate of mandelonitrile. This latter structure was confirmed by synthesis; when equal molecular proportions of benzoyl cyanide and mandelonitrile were heated under similar conditions a yield of nearly 80% of mandelonitrile benzoate was obtained.

$$C_6H_5COCN + C_6H_5{-}CHOH{-}CN{=}C_6H_5{-}CH(O{-}CO{-}C_6H_5)(CN) + HCN \quad (7)$$

The expected rupture of benzilo-dicyanohydrin, according to Equation 6, therefore, takes place, and is followed by ester formation. It is interesting to note the slight temperature difference between that required for the formation of benzilo-dicyanohydrin, and that for its complete decomposition. A mixture of benzil and anhydrous hydrocyanic acid, heated to 90–

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[5] (a) Zinin, *Ann.*, **34,** 189 (1840). (b) Jacoby, *Ber.*, **19,** 1519 (1886).

[6] Beilstein's "Handbuch" quotes Zinin as given here; but Zinin actually wrote only that he obtained *an odor* of ethyl benzoate, and that mercury was reduced. These observations are qualitatively correct, but quantitatively of no significance. Ethyl benzoate is formed slowly when the cyanohydrin is boiled with alcohol alone; and the reduction of a very small amount of mercury appears to come from impurities in the solvent. One must be careful, working in this field, not to mistake the odor of ethyl benzoate for its substance. The sense of smell can detect minute traces which escape the other senses.

100°, gives an excellent yield of cyanohydrin; the same mixture heated to 120° gives chiefly the ester just described, some tar, and a little unchanged benzil.

Benzil is not known to form a monocyanohydrin. Yet it seems probable that the high velocity of Jourdan's reaction is due to the intermediate position of mono- rather than of dicyanohydrin. The dicyanohydrin, covered with alcohol to which a little sodium hydroxide had been added, stood at room temperature overnight without giving any evidence of change.

Discussion

In view of the comparative indifference of benzilo-dicyanohydrin, it seems advisable to assume that the monohydrin is the active intermediate in the reactions briefly described above. The behavior of benzilo-cyanohydrin closely resembles that of benzil sodium ethoxide; both substances rupture, and do not rearrange; but the cyanohydrin, $C_6H_5—CO—C(C_6H_5)(CN)(OH)$, shares with benzil sodium hydroxide, $C_6H_5—CO—C(C_6H_5)(ONa)(OH)$, an hydroxyl group which is lacking in benzil sodium ethoxide, $C_6H_5—CO—C(C_6H_5)(ONa)(C_2H_5)$. We should, therefore, expect the cyanohydrin to undergo rearrangement, rather than to rupture. It will be remembered that benzil sodium hydroxide resists rupture even when fused with an excess of caustic soda; benzilic acid is almost the sole product[7] of this violent operation.

A possible explanation of the contradictory behavior of benzilo-cyanohydrin is suggested by the valuable studies of Lapworth[8] on the mechanism of cyanohydrin formation. Lapworth has shown that the addition of hydrocyanic acid to carbonyl must be regarded as the addition of cyanogen ion to form a complex ion. The production of such a complex ion has been demonstrated experimentally by Bredig and Stern,[9] in the case of mandelonitrile, and Lapworth found that mandelonitrile is formed almost instantly when benzaldehyde is shaken with a solution of potassium cyanide.

We are, therefore, justified in assuming the rapid formation of a similar benzilo-cyano ion when potassium cyanide is added to a solution of benzil.

$$C_6H_5—CO—CO—C_6H_5 + KCN = C_6H_5—CO—C(C_6H_5)(CN)O^- + K^+ \qquad (8)$$

Entirely similar ions, in all probability, exist in the solution of benzil sodium ethoxide in alcohol, $C_6H_5—CO—C—(C_6H_5)(OC_2H_5)O^-$, and also in the solutions which benzil forms with water and with sodium hydroxide, $C_6H_5—CO—C(C_6H_5)(OH)O^-$. Of these three ions, only the last, the benzilohydroxide ion contains an hydroxyl group; benzilo-ethoxide ion, lacking this group, behaves exactly as does benzilocyano ion, which also contains no hydroxyl.

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[7] E. Fischer, *Ber.*, **14**, 326, footnote (1881).

[8] Lapworth, *J. Chem. Soc.*, **83**, 995 (1903); **85**, 1206 (1904); **89**, 945 (1906).

[9] Bredig and Stern, *Z. Elektrochem.*, **10**, 582 (1904). Stern, *Z. physik. Chem.*, **50**, 513 (1904).

If this explanation is correct, the conversion of benzil into benzilic acid, by way of benzilohydroxide ion, is an *intra-ionic* reaction.

$$C_6H_5—CO—C(C_6H_5)(OH)O^- = C_6H_5(C_6H_5)C(OH)—CO—O^- \qquad (9)$$

The rupture reactions of benzilocyano and -ethoxide ions, on the other hand, require the addition of an outside agent, either water or alcohol.

$$C_6H_5—CO—C(C_6H_5)(CN)O^- + HOH = C_6H_5CHO + C_6H_5CO(CN) + OH^- \qquad (10)$$

$$C_6H_5COC(C_6H_5)(OC_2H_5)O^- + HOC_2H_5 = C_6H_5CHO + C_6H_5CO(OC_2H_5) + OC_2H_5^+ \qquad (11)$$

There are some difficulties in the way of this ionic hypothesis. Thus, benzilo-dicyanohydrin (Equation 6), if ionized as above indicated, still contains an hydroxyl group, so that we must assume that *both* cyanohydrin groups are ionized; for this assumption the indifferent behavior of the substance affords no warrant. A more serious objection is found in the failure of benzilohydroxide ion to undergo rupture, except in traces.

$$C_6H_5—CO—C(C_6H_5)(OH)O^- = C_6H_5CHO + C_6H_5CO—O^- \qquad (12)$$

Under the most varied conditions of temperature and alkali concentration, over 95% rearranges according to Equation 9. It is not likely that the great preponderance of rearrangement is solely a question of the relative velocities of the two reactions, for the rupture process of Equation 10, for example, is much more rapid than the rearrangement shown in Equation 9.

For the reasons just given it may be preferable, in the present state of our knowledge, to regard the hydroxyl group of the addition products of benzil as a *necessary* but not *sufficient* condition of rearrangement.

It was hoped that a study of the action of acids on benzil would shed further light on the problem; but when benzil was heated for several hours at 100° with 85% sulfuric acid, in which it dissolves, there was no action; a similar negative result was obtained when it was digested with 25% sulfuric acid at 175° for 18 hours.

Experimental Section

The Action of Potassium Cyanide on Benzil.—A mixture of 5 g. of benzil, 5 cc. of absolute alcohol and 0.5 g. of potassium cyanide was shaken. Reaction was completed within 5 minutes. No benzilic acid was found, and none was obtained after hydrolyzing the ethyl benzoate. After 5 g. of benzil, 20 cc. of absolute alcohol and 1.5 g. of potassium cyanide (the latter added as a single lump) were shaken for 2 minutes, the liquid was poured off; the cyanide fragment had not visibly diminished in size. The reaction mixture, after dilution with ether, was extracted with bisulfite. No unchanged benzil was found. Benzilic acid was absent.

A mixture[10] of 10 g. of benzil, 100 cc. of absolute alcohol and 7.5 g. of potassium cyanide was allowed to stand without shaking for 15 minutes at room temperature. The liquid was then decanted from undissolved cyanide, and a slight excess of bisulfite added. After the alcoholic ester solution had been separated from the precipitate which had formed it was hydrolyzed by cold sodium hydroxide. The benzoic acid obtained weighed 5.1 g., and was entirely free from benzilic acid.

A mixture of 10 g. of benzil, 25 cc. of alcohol, 75 cc. of water and 3.5 g. of potassium cyanide was stirred for 1.5 hours. A slight excess of sodium bisulfite was then added,

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[10] These proportions are the same as those used by Michael and Palmer, Ref. 3.

and the mixture extracted with ether. From the bisulfite solution 1.5 g. of benzaldehyde was obtained. The ether solution was extracted with sodium carbonate; from this 0.45 g. of benzoic acid was isolated, which gave no test for the presence of benzilic acid. Evaporation of the ether solution left 8.6 g. of oil which was a mixture of ethyl benzoate and mandelonitrile. The oil was heated under a reflux condenser until no more hydrocyanic acid was given off; benzaldehyde was then removed with bisulfite, and the residual ester hydrolyzed in the cold as before; 4.9 g. of benzoic acid, free from benzilic acid, was obtained.

Ten g. of benzil was stirred with 100 cc. of water and 5 g. of potassium cyanide. After 3 hours no more benzil crystals were visible, their place having been taken by a yellow oil. This oil, after treatment with ether and bisulfite, gave 2.8 g. of unchanged benzil, and some mandelonitrile which was not examined further. The original aqueous liquor after removal of the oil gave 3.3 g. of benzoic acid, again entirely free from benzilic acid.

Action of Hydrocyanic Acid and Alcohol on Benzil.—Three g. of benzilo-dicyanohydrin was heated, in a sealed tube, with 20 cc. of alcohol for 18 hours at 95°. Reaction was complete; no unchanged benzil was found.

Five g. of dicyanohydrin was heated with 5 cc. of alcohol, for 24 hours at 87–90°; 1 g. of benzil was recovered.

Twenty g. of benzil, 3 g. of anhydrous hydrocyanic acid and 15 cc. of alcohol were heated for 24 hours at 125°. The reaction mixture was distilled in a vacuum and gave 14 g. of oil, which was refractionated at atmospheric pressure; 10 g. of ethyl benzoate, boiling at 205–210°, was obtained.

Action of Benzoyl Cyanide on Alcohol.—2.8 g. of benzoyl cyanide, which had been prepared according to the method of Claisen,[11] was added to 20 cc. of alcohol containing 0.2 g. of potassium hydroxide. The mixture warmed immediately, and a precipitate settled which proved to be potassium cyanide. The liquid was filtered, and evaporated in a vacuum; it left an oily residue which weighed 3.1 g.; calc. for ethyl benzoate, 3.2 g. The oil was hydrolyzed, and gave 2.3 g. of benzoic acid; m. p., 122°.

Benzilo-dicyanohydrin.—Five g. of benzil was heated to 95–100° with 5 cc. of anhydrous hydrocyanic acid. White crystals soon formed, and after 6 hours the tube was cooled, the excess of hydrocyanic acid blown off, and the crystals were washed with cold benzene to remove benzil; 5.6 g. of dicyanohydrin was obtained; calc. 6.3 g.

The best method of preparing quantities of 25–30 g. is to place the tube in a boiling water-bath, so that about $^1/_2$ projects. The hydrocyanic acid boils vigorously, and stirs the tube contents; the cyanohydrin deposits as formed.

A mixture of 2.6 g. of benzilo-dicyanohydrin with 4.4 g. of mercuric oxide and 25 cc. of alcohol was boiled, and darkened after a short time. After 1 hour, more alcohol was added and the liquid filtered hot. The filter residue, which according to Zinin should consist largely of metallic mercury, was almost completely soluble in dil. acetic acid. The hot alcohol filtrate, on cooling, deposited crystals of mercuric cyanide which were not weighed. The alcohol solution was evaporated in a vacuum, and the residue extracted with cold benzene; from the extract 1.9 g. of benzil was recovered; calc., 2.1 g.

Five g. of benzilo-dicyanohydrin was boiled under a reflux condenser with 100 cc. of water. Hydrocyanic acid passed off at once. After 1 hour the mixture was cooled and filtered. The yellow, air-dry solid weighed 3.93 g.; calc. for benzil, 3.98 g.; m. p., 94°.

Two g. of dicyanohydrin was covered with 5 cc. of alcohol, and 1 cc. of 0.5 *N* sodium hydroxide solution was added. The mixture was shaken at frequent intervals for 2 hours, but no odor of ethyl benzoate could be detected. It was then allowed to stand overnight; a slight odor of the ester was noted, but there was no change in the appearance

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[11] Claisen, *Ber.*, 31, 1024 (1898). Benzoyl cyanide boils at 85° at 10 mm.

of the mixture. Finally, it was heated on the water-bath for a few minutes; a strong odor of ethyl benzoate developed.

The experiment was repeated with 20 cc. of methyl alcohol, in which the cyanohydrin was moderately soluble; to this was added 10 cc. of *N* potassium hydroxide solution containing methyl alcohol. After standing for 2 hours at 16° the mixture was acidified with a slight excess of glacial acetic acid, and evaporated in a vacuum. No definite evidence of the presence of either benzaldehyde or ethyl benzoate could be secured.

The Action of Anhydrous Hydrocyanic Acid on Benzil at Higher Temperatures. Mandelonitrile Benzoate.—Thirty g. of benzil and 10 g. of hydrocyanic acid were heated to 140° for 40 hours. The tube contents, when cool, consisted of a black, viscous mass. It was directly distilled in a vacuum; the first portion of the distillate consisted of a little benzil; this was followed by 18 g. of a colorless oil, boiling constantly at 200° at 10 mm. This was refractionated at 5 mm. pressure, at which it boiled at 178°. The oil solidified when the walls of the container were scratched.

The experiment was repeated, and the mixture heated to 125° for 48 hours. The distillate was twice recrystallized from warm methyl alcohol, giving 15 g. of the purified material.

The proof that this substance is the benzoic ester of mandelonitrile was given by the following synthesis from benzoyl cyanide and mandelonitrile. A mixture of 8 g. of each was sealed and heated to 120° for 20 hours. On distillation, 11.5 g., boiling at 175–180° at 5 mm. was obtained, a yield of 80%. On recrystallization from methyl alcohol the synthetic product melted at 61°, as did the original material; this melting point was unchanged when the lots were mixed.

Analyses. Subs., 0.2655, 0.1168: H_2O, 0.1038, 0.0471. Subs., 0.1838, 0.1678: (Kjeldahl) 7.3, 6.4 cc. of 0.1 *N* hydrochloric acid. Calc. for $C_{15}H_{11}O_2N$: H, 4.6; N, 5.9. Found:[12] H, 4.4, 4.5; N, 5.6, 5.4.

Properties.—Mandelonitrile benzoate is very soluble in warm methyl alcohol, only slightly soluble cold, very soluble in benzene, glacial acetic acid, ether, or cold conc. sulfuric acid, insoluble in ligroin; m. p., 61°. The boiling points are given above. Heated at atmospheric pressure in a bath, it gives off gas at 280–285°. It is but slightly affected by prolonged boiling with moderately diluted hydrochloric acid; but when it is warmed with 85% sulfuric acid, all of its nitrogen is removed as ammonia. When boiled with aqueous 6 *N* sodium hydroxide solution, it gives off ammonia very slowly and the odor of benzaldehyde may be noted; the alkaline solution contains benzoic acid. Addition of sodium ethoxide immediately gives an odor of ethyl benzoate and splits off cyano ion.

The Action of Sulfuric Acid on Benzil.—Two g. of benzil was heated in a water-bath with 5 cc. of 85% sulfuric acid for 4 hours. A dark brown solution resulted which solidified on cooling. When this mass was rubbed with cold water it gave a yellow powder which melted at 94° and was unchanged benzil. It weighed 1.8 g.; there were some losses in handling.

Ten g. of benzil was sealed with 25 cc. of 6 *N* sulfuric acid, and heated to 175° for 18 hours. The tube contents were then boiled for a few minutes with an excess of sodium carbonate, cooled, and carefully filtered. The collected benzil weighed 10 g. ± 0.1 g.; m. p., 94.5°. The sodium carbonate liquor was concentrated on the water-bath and finally tested for benzilic acid, of which no trace was found.

Summary

1. Hydrocyanic acid and potassium cyanide act upon alcoholic benzil solutions with the formation of ethyl benzoate and benzaldehyde.

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[12] The carbon determinations were lost because of a defective absorption tube.

2. This rupture process goes through benzilo-cyanohydrin, which breaks down into benzaldehyde and benzoyl cyanide; the latter produces ethyl benzoate as a secondary reaction product.

3. No benzilic acid is formed during the above reaction, in spite of the presence of an hydroxyl group in benzilo-cyanohydrin.

4. On the reasonable assumption that benzilo-cyanohydrin is ionized, it is shown that the ion contains no hydroxyl.

5. It is also possible to account for the non-formation of benzilic acid in the above reaction, on the assumption that some other factor, in addition to the presence of hydroxyl groups in the molecule, is required.

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THE BENZIL REARRANGEMENT. IV. BENZOIN

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Received February 10, 1923

In several recent papers the factors which determine the rearrangement of benzil into benzilic acid have been studied. The present paper deals with the behavior of benzoin, a closely related substance.

The Action of Heat on Benzoin

When heated above 200°, benzoin readily loses hydrogen and forms benzil.

$$C_6H_5—CH(OH)—CO—C_6H_5 = C_6H_5—CO—CO—C_6H_5 + H_2 \qquad (1)$$

When metallic palladium is present, hydrogen is given off as such; otherwise, it acts upon benzoin itself to yield various reduction products. Mild oxidizing agents, such as Fehling solution, and even atmospheric oxygen (when alkalies are present) also result in the production of benzil[1] at or below 100°.

Benzoin when heated also gives considerable benzaldehyde, evidently as a reversal of its synthesis; this reaction is favored at atmospheric pressure. Engler and Grimm further noted the formation of diphenylmethane, $C_6H_5—CH_2—C_6H_5$. They give a curiously involved explanation of its production, which need not be discussed here; a more reasonable mechanism is given later in the present paper.

The Action of Hydrocyanic Acid on Benzoin

Benzoin is formed by the action of cyanides, or rather by that of cyano ion, on benzaldehyde;[2] the mechanism of this condensation is far from being

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[1] Engler and Grimm, *Ber.*, **30,** 2921 (1897). Knoevenagel and Arndts, *ibid.*, **35,** 1982 (1902). The reduction products obtained when benzoin is heated are hydrobenzoin, $C_6H_5—CH(OH)—CH(OH)—C_6H_5$, toluylene hydrate $C_6H_5—CH_2—CH(OH)—C_6H_5$ and desoxybenzoin, $C_6H_5—CH_2—CO—C_6H_5$.

[2] Liebig and Wöhler, *Ann.*, **3,** 266 (1832). Zinin, *ibid.*, **34,** 189 (1840). Lapworth, *J. Chem. Soc.*, **83,** 995 (1903); **85,** 1206 (1904); **89,** 945 (1906). Bredig and Stern, *Z. Elektrochem.*, **10,** 582 (1904). Stern, *Z. physik. Chem.*, **50,** 513 (1904). Staudinger, *Ber.*, **46,** 3535 (1913). Refer also to Smith, *Am. Chem. J.*, **22,** 253 (1899).