

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

THE BENZIL REARRANGEMENT. IV. BENZOIN

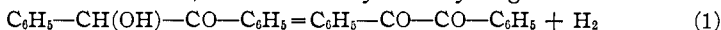
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In several recent papers the factors which determine the rearrangement of benzil into benzoic acid have been studied. The present paper deals with the behavior of benzoin, a closely related substance.

The Action of Heat on Benzoin

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



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 alkalis are present) also result in the production of benzil¹ 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, $\text{C}_6\text{H}_5-\text{CH}_2-\text{C}_6\text{H}_5$. 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

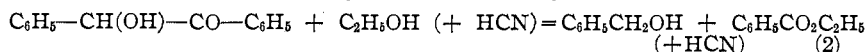
Benzoin is formed by the action of cyanides, or rather by that of cyano ion, on benzaldehyde;² the mechanism of this condensation is far from being

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, $\text{C}_6\text{H}_5-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{C}_6\text{H}_5$, toluylene hydrate $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}(\text{OH})-\text{C}_6\text{H}_5$ and desoxybenzoin, $\text{C}_6\text{H}_5-\text{CH}_2-\text{CO}-\text{C}_6\text{H}_5$.

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).

understood. Stern has shown that with increasing proportions of catalyst, less benzoin is formed; and that benzoin itself is partially, and slowly, used up, benzaldehyde appearing among the products of reaction.³

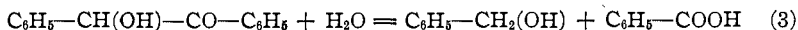
The comparative stability of benzoin towards cyano ion stands in sharp contrast to the behavior of benzil, which is instantly⁴ ruptured into benzoyl cyanide and benzaldehyde, by very small amounts of alkali cyanides. Anhydrous hydrogen cyanide seems to have no action on benzoin. Alcoholic hydrocyanic acid, on the other hand, which acts readily upon benzil to form benzaldehyde and ethyl benzoate, also reacts with benzoin in a similar manner, forming benzyl alcohol and ethyl benzoate,⁵



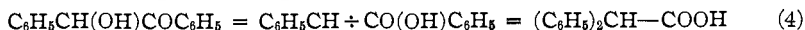
and it seems likely that the mechanism is the same as with benzil, namely, that benzoyl cyanide is the intermediate product.⁵

The Action of Alkalies on Benzoin

The action of aqueous alkalies on benzoin has received careful study in the past. Klinger⁶ boiled benzoin with a great excess of 1.3 *N* potassium hydroxide solution; when air was excluded he noted almost quantitative recovery of benzoin; in the presence of a current of air, oxidation to benzil took place, followed by production of benzilic acid. Knoevenagel and Arndts¹ extended this investigation; no action was observed at 100°, with alkali up to 7 *N*; above these limits, rupture into benzyl alcohol and benzoic acid took place:



I have repeated this work, with the object of searching for a possible rearrangement, similar to that of benzil. A rearrangement, in the case of benzoin, should produce diphenylacetic acid.



No evidence of such a reaction, under these conditions, was observed.⁷

³ Since the above was written, Anderson and Jacobson, *THIS JOURNAL*, **45**, 836 (1923), have published an incomplete study of this reaction, without reference to the work of Stern. Stern's data show that no true equilibrium between benzaldehyde and benzoin exists.

⁴ Compare Lachman, *THIS JOURNAL*, **45**, 1509 (1923).

⁵ This reaction has been studied by Michael and Palmer, *Am. Chem. J.*, **7**, 193 (1885). These authors assume that benzoin is first ruptured into benzaldehyde, and that this substance reacts, in a manner which is not discussed, to yield ethyl benzoate. As shown in the experimental section of the present paper, benzoin and benzaldehyde were separately heated under identical conditions with alcoholic hydrocyanic acid. No ethyl benzoate could be obtained from benzaldehyde.

⁶ Klinger, *Ber.*, **19**, 1868 (1886).

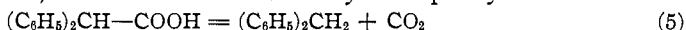
⁷ The solubility of diphenylacetic acid, in hot and in cold water, is such that a separation from benzoic and from benzilic acid offers no difficulties; even a few centigrams can be isolated.

Benzil has recently been shown⁸ to form a well-defined addition product with sodium ethoxide, which breaks down into benzaldehyde and ethyl benzoate. Benzoin forms a similar addition product, which has not yet been obtained in a pure state as it carries considerable adhering or adsorbed mother-substance. It breaks down, at least in part, into benzyl alcohol and ethyl benzoate.

Formation of Diphenylacetic Acid

It was possible to effect the "benzoin rearrangement" into diphenylacetic acid, according to Equation 4, when benzoin was acted upon by acids at high temperatures. The acids so far employed have been sulfuric and phosphoric; a variation of concentration between M and $6 M$ has not had much effect on the yield. Time and temperature are more important factors.

The reaction is complicated by various side processes. At the necessary temperature, 200–250°, the heat reactions already described take place. Sulfuric acid accelerates the oxidation of benzoin into benzil, being reduced to hydrogen sulfide. These reactions are faster than the rearrangement, and thus serve to withdraw benzoin from the amount available for the latter possibility. Finally, diphenylacetic acid itself is not very stable under the given conditions; it loses carbon dioxide to yield diphenylmethane.

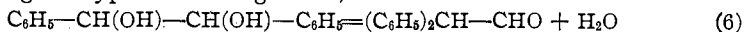


The best yield of diphenylacetic acid, actually isolated so far, has been about 9%.

The occurrence of diphenylmethane and carbon dioxide among the products obtained by Engler and Grimm when they heated benzoin in sealed tubes may be accounted for readily on the basis of the facts presented here. The necessary steps are isomerization (Equation 4), and loss of carbon dioxide (Equation 5).

Discussion of Results

It is interesting to compare the metaklinic⁹ process as it occurs with the three closely related substances hydrobenzoin, benzoin, and benzil. Hydrobenzoin is a glycol, and under the influence of acids loses water while undergoing the typical rearrangement,¹⁰



with formation of diphenylacetaldehyde.

Benzoin, also under acid catalysis, rearranges into diphenylacetic acid *without losing or gaining* water. Alkaline catalysis of benzoin results in rupture into benzyl alcohol and benzoic acid, with addition of water.

Benzil, finally, rearranges under alkaline catalysis with *addition* of water.

⁸ Lachman, *THIS JOURNAL*, **45**, 1509 (1923).

⁹ *Ibid.*, **44**, 338 (1922).

¹⁰ Breuer and Zincke, *Ann.*, **198**, 151 (1879). Tiffeneau and Orékhoff, *Compt. rend.*, **171**, 400 (1920). Breuer and Zincke employed 20% sulfuric acid at 100°. An anhydride of hydrobenzoin is formed at the same time.

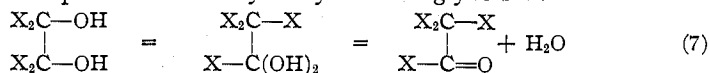
Alkaline catalysis in the absence of water causes rupture, without rearrangement. Acids have no action whatever.

TABLE I
METAKLINY OF BENZIL, BENZOIN AND HYDROBENZOIN

Catalyst ion	Benzil	Benzoïn	Hydrobenzoïn
H ⁺	no action	rearrangement	loss of water, rearrangement
OH ⁻	addition of water rearrangement very little rupture	addition of water rupture no rearrangement	no action
OR ⁻	addition of alcohol rupture no rearrangement	addition of alcohol rupture	no action
Water only	addition of water rearrangement	no action	no data at hand

No theory of rearrangement such as that of Tiffeneau¹¹ is adequate, which has as its basis the formation of unsaturated valences by *loss* of water. The facts tabulated above agree much better with the assumption of a mobile hydroxyl group, capable of exchanging places with phenyl.

The typical equation for the hydroxyl shift in glycols is:



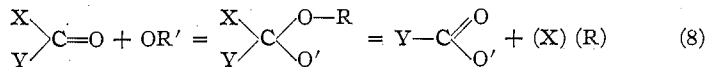
where X may be any atom or radical. When the 4 atoms represented here by X differ among themselves, preferences as to which shall exchange places with —OH may be manifested.^{12,13}

¹¹ Tiffeneau, *Rev. gén. sci.*, **18**, 584 (1907). For a more detailed discussion, cf. Lachman, *THIS JOURNAL*, **44**, 336 (1922).

¹² For the further understanding of this metaklinic process, it is important to determine the rules that govern these preferences. In many cases phenyl wanders more readily than hydrogen, even though this involves a rearrangement of the carbon chain. This phase of the problem is being studied effectively by Tiffeneau and by Meerwein.

¹³ It seems probable that the driving force in this intramolecular oxidation-reduction is not the free energy of formation of water, but rather the tendency of the carbonyl group, =C=O, to form. It is well known that practically no heat is developed when an organic acid combines with an alcohol with elimination of water. On the other hand, the carbonyl group is formed, and persists, in such a variety of reactions, that we must assign to it a high degree of stability. Thus we have the production of pyruvic acid when tartaric acid solutions are boiled; the formation of acetaldehyde from acetylene and water; the conversion of lactic acid into acetaldehyde and carbon monoxide, when heated with sulfuric acid; the production of benzophenone when benzilic acid is boiled with water, or exposed to sunlight. The catalytic air oxidation of methyl and ethyl alcohol tends to stop at the aldehyde stage. Dibenzyl ether, when warmed, produces benzaldehyde and toluene. The oxidation of protein in the animal organism stops at urea, (NH₂)₂C=O. Ozonides of the hydrocarbons are converted into aldehydes by the action of water. It should also be pointed out that a separation of the hydroxyl groups, as in the β-glycols, is no barrier to the shifting process; 1,3-butandiol, CH₃—CHOH—CH₂CH₂OH, goes over into a mixture of the two possible metaklinic products, CH₃—CH₂—CH₂—CHO and CH₃—CO—CH₂—CH₃.

The glycol shift is catalyzed chiefly by acids, and results in the production of a carbonyl group. Alkaline catalysis, by contrast, acts upon carbonyl groups to produce the *carboxyl ion*. Here also we may write a general equation,



X and Y may be any groups; R is hydrogen or alkyl. For its completion, this process requires the separation of the bond between X and C; the groups X and R may either find a place within the same molecule, as in the benzoic acid rearrangement, or they may be completely ruptured, as when benzoic acid breaks into benzyl alcohol and benzoic acid. If R adheres firmly to its oxygen atom, X may separate alone; this seems to be the case with benzil sodium ethoxide, which was described recently. Just as with the glycols, the nature of X, Y and R determines whether the process shall terminate in rupture or in rearrangement.

Lack of space prevents further consideration of Equations 7 and 8. Analogous considerations probably hold in those oxidation-reduction processes which are catalyzed by cyanide ion. It should be pointed out, however, that the conversion of benzoic acid into diphenylacetic acid, by hydrogen ion catalysis, is somewhat anomalous.

For easy reference, the action of cyanide ion, etc., on benzil, benzoic acid and benzaldehyde, are here tabulated.

TABLE II

ACTION OF CYANIDE ION ON BENZIL, BENZOIN AND BENZALDEHYDE			
Catalyst	Benzil	Benzoic acid	Benzaldehyde
Anhydrous HCN	addition (100°) rupture (120°)	no action	addition
HCN in alcohol	rupture	rupture	addition
Cyanide ion, low concentration	immediate rupture cold	little action	condensation to benzoic acid
Cyanide ion, high concentration	same	slow reversal of condensation	addition to form mandelonitrile

To the data tabulated in Tables I and II there should be added Cannizzaro's reaction: under the influence of hydroxyl ion, 2 molecules of benzaldehyde undergo mutual oxidation and reduction. One is oxidized to benzoic acid; the other is reduced to benzyl alcohol. This reaction is being studied, and the results will be published soon.

Experimental Section

Action of Anhydrous Hydrocyanic Acid.—Benzoic acid is very soluble in hot anhydrous hydrogen cyanide; when the tubes are cooled, it crystallizes in beautiful, feathery masses. Five g. of benzoic acid was heated with 5 cc. of hydrogen cyanide for 72 hours at 90–100°. After it had cooled, the colorless acid was poured off and evaporated; the residue it left melted at 128° (133° after recrystallizing from alcohol). The tube contents consisted of unchanged benzoic acid; total recovery, 4.8 g. The experiment was repeated, but 4 hours'

heating at 125–130° caused no evident action. Five hours' heating at 145° resulted in a dark brown liquid, which was carefully distilled in a vacuum; aside from a black tar, the only product obtained was benzoin. A final lot was heated to 175° for 1 hour; this gave a solid black tar from which nothing could be distilled; the tube contained ammonia gas under considerable pressure.

If benzoin showed the same behavior towards hydrocyanic acid that is evidenced by benzil, the rupture products would be benzoyl cyanide and benzyl alcohol, and these might combine to form benzyl benzoate. No benzyl benzoate could be found.

Benzoin, Hydrocyanic Acid and Alcohol.—A mixture of 25 g. of benzoin, 8 g. of hydrocyanic acid, and 15 cc. of absolute alcohol was heated to 130° for 40 hours. Tube contents were dark; a slight pressure was noted; a faint odor of ammonia was evident. On distillation, after removal of alcohol, a small amount of a solid passed over which proved to be benzamide. Subsequently, 2.2 g. of ethyl benzoate was isolated; b. p., 208–210; from this 1.9 g. of benzoic acid was obtained.

A mixture of 20 g. of benzoin, 3 g. of hydrocyanic acid and 15 cc. of absolute alcohol was heated for 18 hours at 150°. After separation from benzamide as before, 8 g. of oil was obtained. From this, 2.5 g. of benzoic acid was separated by hydrolysis with alcoholic sodium hydroxide; from the hydrolyzed liquid after extraction with ether 4 g. of benzyl alcohol was isolated; b. p., 205–208°.

Benzaldehyde, Hydrocyanic Acid, and Alcohol.—Along with the benzoin experiments just described, similar tubes, containing benzaldehyde instead of benzoin, were heated. In neither case was any ethyl benzoate obtained. From the second tube, 0.9 g. of a solid product, melting at 230°, was separated; this substance gave ammonia when boiled with concd. sodium hydroxide solution.

A third tube, containing 20 g. of mandelonitrile and 20 cc. of alcohol, was heated to 180° for 8 hours, again without production of ethyl benzoate.

Action of Sodium Ethoxide on Benzoin.—Two g. of benzoin was dissolved in 75 cc. of absolute alcohol, 45°; to this was added 10 cc. of 1.7 *N* sodium ethoxide solution. The mass set to a solid cake within 1 minute. It was packed in ice for 30 minutes, then filtered and washed with 50 cc. of absolute alcohol. The product was a white, asbestos-like, voluminous mass, and weighed 1.7 g. On titration with hydrochloric acid it was found to contain 5.05% of free alkali, calculated as sodium ion. The corresponding number for an addition product of 1 mole each of benzoin and sodium ethoxide is 8.22%. After titration the insoluble benzoin residue was washed with water and weighed; 88% of benzoin was found; calc., 76%.

Two g. of benzoin was dissolved in 400 cc. of dry ether and precipitated with sodium ethoxide, as above. The cake weighed 2.3 g., and contained 3.6% of sodium ion; it also contained 50.1% of benzoin and 33.4% of sodium benzoate.

The filtrates from the above cakes gave strong odors of ethyl benzoate which disappeared on standing. In one case, where an excess of sodium ethoxide was avoided, 0.5 g. of ethyl benzoate was isolated.

Production of Diphenylacetic Acid.—The following table gives in brief form a few of the results obtained when benzoin was heated with sulfuric and with phosphoric acid. In each case, 10 g. of benzoin and 25 cc. of acid were heated in sealed tubes. The reaction mixture was subsequently boiled for about 30 minutes with a slight excess of sodium carbonate solution, then cooled and filtered. Sodium hydroxide must not be used, as benzil is always present. The filtered solution is acidified with a slight excess of mineral acid; diphenylacetic acid is precipitated at once and may be recrystallized from boiling water with practically no loss. As obtained in this way, various samples melted at 147°. The mother liquors were in five instances extracted with ether to determine (a) any loss of diphenylacetic acid, (b) presence of benzilic acid and (c) presence of benzoic acid. The loss of diphenylacetic acid was negligible; no benzilic acid was ever

found; benzoic acid appeared twice in amounts too small to isolate, but recognizable by means of the ferric chloride precipitate.

The various reduction products of benzoil which are simultaneously formed were not separately estimated, but in several instances the amount of unchanged benzoil was determined by washing the sodium carbonate filter residue with ether, in which benzoil is but slightly soluble (about 0.3 g. per 100 cc. in dry ether). When sulfuric acid is used, the tubes smell strongly of hydrogen sulfide.

TABLE III
FORMATION OF DIPHENYLACETIC ACID

Acid	Strength <i>M</i>	Temperature C.	Time Hrs.	Diphenyl- acetic acid G.	Benzoil recovered G.
H ₂ SO ₄	1.5	175	4
	3.0	175	4
	5.0	175	4	0.06	...
	3.0	175	18	0.10	8.0
	5.0	180	18	0.25	3.6
	1.5	230	4	0.80	5.0
H ₃ PO ₄	6.0	175	65	0.45	8.25
	2.0	200	42	0.35	...
	2.0	230	5	0.15	...
	6.0	230	5	0.25	...
	6.0	230	66	0.90	2 g. of diphenylmethane

In the last case considerable pressure was noted; the gases contained carbon dioxide. The sodium carbonate residue was extracted with ether; the ether was evaporated, and this residue extracted with a little cold ligroin. The ligroin residue was oxidized with chromic acid mixture to convert diphenylmethane into benzophenone and the latter was transformed into its oxime, which was found to weigh 2.2 g. No unchanged benzoil was found.

Two different lots of diphenylacetic acid were analyzed.

Analyses. Subs., 0.2475, 0.4951: 11.55, 23.30 cc. of 0.1 *N* sodium hydroxide. Calc. for C₁₄H₁₂O₂, 11.65, 23.35 cc.

Summary

1. A comparison is made between the action of various reagents on benzoil and on benzil.
2. Benzoil is shown to rearrange into the isomeric substance diphenylacetic acid.
3. Unlike benzil, this rearrangement is catalyzed only by acids.
4. The significance of these facts and their application to the general theory of rearrangements are discussed.

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