4. Evidence is given that the acid melting at 121–122° is *l-trans*-3-hydroxy-1,5,5-trimethyl-cyclopentanoic acid.

5. Evidence is given that the acid melting at 210° is *i*-2-hydroxy-1,5,5-trimethyl-cyclopentanoic acid.

6. The lactones of the 2 dihydroxy acids derived from the unsaturated acids have been prepared and their properties studied.

7. The esters of the unsaturated and hydroxy acids undergo some racemization in their formation from the ester of the amino acid.

8. Some suggestions have been made which afford a partial explanation of the course of the reaction.

The study is being continued with a view to learning the mechanism of the diazo reaction in various types of compounds especially from the standpoint of the products formed. The properties of the diazo compounds themselves will be reported as soon as these compounds can be purified.

Madison, Wisconsin

[Contribution from the Chemical Laboratory of the University of California]

THE BENZIL REARRANGEMENT. II

By Arthur Lachman

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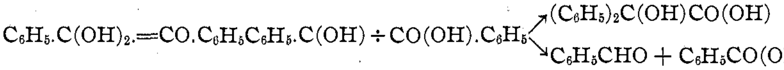
In a recent study[1] of the rearrangement of benzil to benzilic acid, it was pointed out that this reaction involves the process known as "intramolecular oxidation and reduction." It was also shown that this type of rearrangement, for which the much shorter term *metakliny* was suggested, is always accompanied, in varying degree, by a rupture of the molecule at the same point at which the metaklinic process is occurring.

It was possible to account for both reactions by the assumption of a shifting hydroxyl group. Benzil adds a molecule of water when it goes over into benzilic acid.

$$C_6H_5{-}CO{-}CO{-}C_6H_5 + H_2O = (C_6H_5)_2C(OH)CO.OH \qquad (1)$$

This addition must occur primarily at one of the carbonyl groups, and it is one of the hydroxyl groups thus formed which migrates.[2]



$$C_6H_5.C(OH)_2.{=}CO.C_6H_5C_6H_5.C(OH) \div CO(OH).C_6H_5 \begin{array}{l} \nearrow (C_6H_5)_2C(OH)CO(OH) \qquad (2A) \\ \searrow C_6H_5CHO + C_6H_5CO(OH) \quad (2B) \end{array}$$

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[1] Lachman, (a) This Journal, **44**, 336 (1922). The literature of the benzil rearrangement given there need not be repeated here. An important omission, however, should be rectified. Jena, [(b) *Ann.*, **155**, 78 (1870)] heated 1 g. of benzil with water to 200° for 6 hours, and obtained 0.25 g. of benzilic acid, "very pure."

[2] For the use of the division sign, ÷, to indicate the *incomplete* shift, see Ref. 1a., p. 338. In that paper, the addition of *two* molecules of water to benzil was assumed, in order to make clearer the analogy between benzil and dihydroxy-tartaric acid. It seems more likely, from the data in the present paper, that only 1 molecule of water takes part in the reaction.

Equation 2A shows metakliny; 2B indicates the rupturing process. Both are looked upon as the differing final states of a single initial reaction.

The present paper deals with a study of some of the factors which determine, in the case of benzil, whether the inital reaction shall result in metakliny, or in rupture, or in varying proportions of both.

The Action of Sodium Ethoxide on Benzil

When benzil is dissolved in dry ether, and an alcoholic solution of sodium ethoxide is added, a voluminous crystalline addition product separates almost instantly. This hitherto undescribed substance is composed of 1 molecule of benzil and 1 molecule of sodium ethoxide; when an excess of reagent (2 or more molecular proportions) is taken, the same product is formed. Addition seems to be limited to a single carbonyl group; if the second one also adds, the compound is either too soluble to be isolated, or, as will be shown below, it is unstable.

Benzil sodium ethoxide is a perfectly white substance,[3] which keeps well when protected from moisture. Water decomposes it instantly, and quantitatively, into benzil, sodium hydroxide and alcohol.

$$C_5H_5.C(ONa)\ (OC_2H_5).CO.C_6H_5 + H_2O = C_6H_5.CO.CO.C_6H_5 + NaOH + C_2H_5OH \quad (3)$$

When the substance is allowed to stand in its mother liquor it decomposes very slowly; after 5 days it was possible to recover 85% of the benzil originally taken.

When, however, benzil sodium ethoxide is formed in a mixture of ether with sufficient alcohol to prevent its precipitation, or in absolute alcohol alone, the solution is completely decomposed after standing for 3 to 5 days at room temperature. The products of this decomposition are benzaldehyde and ethyl benzoate; a small amount of sodium benzoate may be noted; *benzilic acid appears only in traces.*

This somewhat unexpected result indicates that water is the factor which determines whether benzil shall undergo metakliny, or rupture. By varying the amount of water, it should be possible to control these processes. Experiment amply confirmed this conclusion. When the solvent contained

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[3] There is much confusion in the literature regarding the color of benzil when dissolved in alcoholic alkalies. Compare Michael [(a) THIS JOURNAL, **42,** 814 (1920)]: "The violet coloration on treating benzil with alcoholic potash is undoubtedly due to the formation of an addition product." The benzil used in the present work was prepared in the customary manner from benzoin, and then reheated for several hours with fresh nitric acid. It was then melted with a slight excess of sodium carbonate solution to remove a yellow acid impurity. Other writers have attributed to benzoin the color noted with impure benzil; but carefully purified benzoin also gives a perfectly white addition product with sodium ethoxide. My own observations lead to the belief that the colors are due to subsequent oxidation, and are in some way related to the formation of the substance called ethyldibenzil, investigated by Jena (Ref. 1b) and by Owens and Japp [(b) *Am. Chem. J.,* **7,** 16 (1885)]. This substance is formed by benzilic acid also, as well as from benzoin.

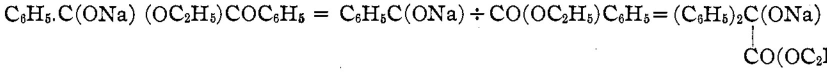
5% of water, 13% of the benzil appeared as benzilic acid; with a little more than 20% of water the yield of benzilic acid jumped to 80%. It was shown, further, that temperature changes up to the boiling point of the solvent did not influence the proportions of benzilic and of benzoic acids found. The details will be found in the experimental section.[4]

Discussion of Results

The structure of benzil sodium ethoxide follows directly from its decomposition by water (Equation 3). The production of ethyl benzoate and of benzaldehyde, in the absence of water, would seem to prove that there is no migration of either the sodium oxide (—ONa) or of the ethoxy group, for if the former shifted, exchanging places with phenyl, the product would be (the sodium salt of) ethylbenzilic acid, but the quantitative data given[5] further on show that no such substance is found.

$$C_6H_5.C(ONa)\ (OC_2H_5).CO.C_6H_5 = C_6H_5C(OC_2H_5) \div CO(ONa).C_6H_5 = (C_6H_5)_2C(CO.ONa)(OC_2H_5) \quad (4)$$

If, on the other hand, we assume that the ethoxy group has migrated, the product formed would be the ethyl ester of benzilic acid (after hydrolyzing its sodium compound).



$$C_6H_5.C(ONa)\ (OC_2H_5)COC_6H_5 = C_6H_5C(ONa) \div CO(OC_2H_5)C_6H_5 = (C_6H_5)_2\underset{\displaystyle CO(OC_2H_5)}{\underset{|}{C}}(ONa) \quad (5)$$

The ester actually obtained was exclusively ethyl benzoate; the acid produced from it by hydrolysis was free even from minute traces of benzilic acid.

We must conclude that metakliny fails to occur with benzil sodium ethoxide. This addition product undergoes rupture only; the evidence at hand so far does not enable us definitely to decide whether the rupturing process is direct.

$$C_6H_5.C(ONa)\ (OC_2H_5)—CO.C_6H_5 = C_6H_5.CO(OC_2H_5) + Na.CO.C_6H_5 \quad (6)$$

or whether it requires the further addition of a molecule of alcohol,

$$C_6H_5.C(ONa)\ (OC_2H_5)COC_6H_5 + C_2H_5OH = C_6H_5.CO.(OC_2H_5) + C_6H_5CHO + C_2H_5ONa \quad (7)$$

Equation 6 involves formation of the entirely unknown sodium compound of benzaldehyde; Equation 7 is able to account satisfactorily for the stability of the solid addition product in the presence of its mother liquor,

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[4] It must be noted that in no case was benzilic acid entirely absent. Using the driest solvents obtainable, but working under ordinary laboratory conditions, the smallest yield of benzilic acid was a little over 2%. If we assume that all of the water that may be present is used up in forming benzilic acid, it would be equivalent to 4 mg. in over 100 cc. of ether, alcohol and sodium ethoxide solution. To exclude so small an amount is a task of such unusual difficulty that it does not seem worth while.

[5] A so-called ethylbenzilic acid has been described by Limpricht and Jena [*Ann.*, **155,** 100 (1870)]. It is a substance of doubtful purity, as it was obtained only as a glassy mass; and it is not soluble in sodium hydroxide solution. It is, therefore, not a true acid, and should be deleted from the list of known compounds.

as compared with its much more rapid decomposition when larger amounts of alcohol are present. The role of sodium ethoxide here, acting to *esterify in alkaline solution*, closely resembles the action of sodium benzylate in the formation of benzyl benzoate from benzaldehyde, as described by Claisen.[6]

In the presence of sufficient water, the formation of sodium ethoxide is greatly repressed, or entirely prevented. Under these circumstances the intermediate addition product formed by benzil is

$$C_6H_5.C(OH)_2.CO.C_6H_5 \qquad (8)$$

or, if sufficient sodium hydroxide is present,

$$C_6H_5.C(OH)\ (ONa).CO.C_6H_5 \qquad (9)$$

In both of these compounds, an hydroxyl group is present and, according to the theory previously advanced, is capable of shifting. It is a striking confirmation of the usefulness of this theory, that in the absence of hydroxyl groups metakliny is not manifested. It should be noted that a small amount of benzoic acid is always formed when benzil is heated with water or with sodium hydroxide solution. Rupture always accompanies metakliny; but the reverse of this statement is not true—metakliny does not always accompany rupture.

The behavior of benzil in the presence of varying amounts of water, alcohol and sodium hydroxide, will be given by the ratio of the rates of the two independent reactions just described.[7] Actual rate measurements of these reactions would be very desirable, but it has not yet been possible to discover a suitable technique. In general, benzilic acid will be almost the sole product until an alcohol concentration of about 80% is reached; after that, the proportion of benzoic acid formed will rapidly increase. A considerable variation in the concentration of sodium hydroxide will not greatly affect the rate ratio. An increase will favor the formation of sodium ethoxide, catalyzing rupture, but it will also increase the formation of the benzil sodium hydroxide addition product, thus also catalyzing metakliny. The influence of temperature changes will be negligible, as both reactions seem to have almost identical temperature coefficients.

The theory of a mobile hydroxyl group as the basis of the rearrangement of benzil is the only one consistent with the experimental facts given in this and in the previous paper. In no other way can we account for the formation of benzilic acid by water alone in the absence of alkali, nor for the failure of benzilic acid to form in the presence of alkali and in the absence of water.[8]

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[6] Claisen, *Ber.*, **20**, 646 (1887).

[7] For a discussion of the significance of rate ratios in considering the products of a given reaction, compare Lachman, THIS JOURNAL, **43**, 2090 (1921).

[8] Since this paper was written, Scheuing [*Ber.*, **56B**, 252 (1923)] has described the additional products which benzil forms with potassium hydroxide, methoxide and ethoxide. He was unable to add more than 1 molecule of these reagents, in agreement with the present data. He also noted the very small production of benzilic acid when water was absent, but the significance of this observation seems to have escaped him.

Experimental Section

Preparation of Benzil Sodium Ethoxide.—(I) To a solution of 5 g. of benzil in 100 cc. of dry ether was added 25 cc. of *N* sodium ethoxide solution in absolute alcohol. A precipitate formed almost immediately and rapidly increased in bulk. It was separated after half an hour (protected from atmospheric moisture during the operation), washed with dry ether, and dried in a vacuum; weight, 4.0 g. (II). The quantities taken were 5 g. of benzil, 100 cc. of ether and 50 cc. of ethoxide solution. The precipitate formed much more slowly. The solid weighed 3.1 g. The ether filtrates from both of these preparations smelled strongly of ethyl benzoate. Both precipitates were pure white.

Analysis of Benzil Sodium Ethoxide.—Weighed samples were dropped into about 50 cc. of cold water, and promptly titrated with 0.1 *N* hydrochloric acid. The neutral liquids were then filtered through a tared paper, and the collected yellow precipitate was washed and dried in a vacuum to constant weight; m. p., 93–94°.

Analyses. Calc. for $(C_6H_5CO)_2.NaOC_2H_5$: Na, 8.3; benzil, 75.6. Calc. for $(C_6H_5CO)_2.2\,NaOC_2H_5$: Na, 13.3; benzil, 60.7. Found: Na, 7.6, 7.7; benzil, 76.4, 73.7.

Decomposition of Benzil Sodium Ethoxide in the Absence of Water.—Two g. of benzil was dissolved in 100 cc. of dry ether and precipitated with 10 cc. of *N* sodium ethoxide solution. After 5 days' standing the originally colorless liquor was pale violet, and the solid, light gray. There were no color changes during the first 3 days. A solution of sodium bicarbonate was then added, and the ether layer evaporated. Benzil weighing 1.7 g. was recovered.

Ten g. of benzil was dissolved in 100 cc. each of dry ether and absolute alcohol, and 50 cc. of *N* sodium ethoxide was added. This corresponded to 1.05 molecular equivalents of the ethoxide. The perfectly clear solution was allowed to stand for 5 days at room temperature. A slight excess of sodium bicarbonate solution was next added, in order to prevent hydrolysis of the esters present. The ether-alcohol layer was concentrated at low temperature in a moderate vacuum to remove the solvents, and the residue distilled at atmospheric pressure. The distillates were refractionated, giving 3.0 g. of benzaldehyde, (b. p., 175–185°), 3.7 g. of ethyl benzoate, (b. p., 205–210°), and 1.0 g. of benzil as residue. The ethyl benzoate when saponified gave 2.9 g. of benzoic acid, m. p. 122°. It was shown to be entirely free from benzilic acid by the extremely sensitive colorimetric method previously described.[9] The sodium carbonate layer was acidified, and gave 3.2 g. of mixed acids. These were recrystallized from boiling water, in which a part was insoluble. The insoluble portion was the so-called ethyldibenzil of Owens and Japp;[10] it weighed 0.4 g., and melted at 196°. As the solution cooled, 2.6 g. of benzoic acid separated; m. p., 121–122°. This gave a distinct color test for benzilic acid. The mother liquors separated from benzoic acid contained 0.15 g. benzilic acid, estimated colorimetrically. The colorimetric method is reliable to ± 5%.

Influence of Water on the Decomposition of Benzil Sodium Ethoxide.—The following table gives the results of a series of experiments in which solvent water and alkali were varied within rather wide limits. In each test 2.1 g. of benzil (0.01 molecular equivalent) was taken. Except as noted, the work was performed at room temperature. In most of the cases, the reaction mixture was worked up, to make sure that little or no benzil was left unchanged. In all the experiments in which the production of benzilic

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[9] Ref. 1a, p. 331, footnote.

[10] Ref. 3b. This substance, during the present work, always appeared in various but small amounts in the alkaline liquors and separated with the acids. But, once separated, it does not redissolve in dilute alkali.

acid was very small, the total acid was weighed; the yield of benzoic acid was always between 1.1 and 1.2 g.; calc., 1.2 g. The benzilic acid production was estimated colorimetrically.

The weight of benzoic acid obtained in these tests proves conclusively the absence of "ethylbenzilic acid" as a reaction product; the molecular weight of this acid is 256, and any appreciable amount present would be indicated by an increase in the weight of the yield of acid, as well as by an influence on the melting point.

Table I

Effect of Water on the Decomposition of Benzil Sodium Ethoxide

	Solvent			Benzilic Acid		
Ether	Cc. alcohol	Water	Mol. eq. NaOEt	G.	%	
..	100	..	0.01	.066	2.9	(5 hrs. at 70°)
..	110	..	1	.062	2.6	(4 days cold)
50	70	..	3	.100	4.4	
50	60	..	1	.050	2.2	
50	60	2	1	.070	3.1	
..	100	5	2	.300	13.1	
..	100	15	2	.580	25.4	
..	90	25	2	1.80	79.1	
..	4	4	0	2.00	87.6	(24 hrs.' agitation)

The proportions taken in the last experiment are those given by H. v. Liebig,[11] for the preparation of benzilic acid with a yield above 90%. Liebig boiled his reaction mixture for 10–12 minutes. The rate of the rearrangement as carried out in the cold, corresponds very closely to the normal temperature coefficient (doubling every 10 degrees).

Summary

1. Benzil forms an addition product with 1 molecule of sodium ethoxide.

2. When treated with water, this addition product breaks down into its components.

3. When allowed to stand in alcoholic solution, in the absence of water, it breaks down into benzaldehyde and ethyl benzoate. Only traces of benzilic acid are formed.

4. When various amounts of water are added to the alcoholic solution, the production of benzilic acid increases rapidly.

5. These results show that hydroxyl groups are a necessary factor in the metakliny of benzil, and that the groups sodium oxy and ethoxy, although similar in chemical character, are incapable of shifting.

6. The theory previously advanced, that the benzil rearrangement is due to a mobile hydroxyl group, is the only one consistent with the experimental facts.

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[11] Liebig, *Ber.*, **41**, 1644 (1908). Liebig cautions against longer heating than he prescribes. The result of such longer heating is to form considerable quantities of the ethyldibenzyl already referred to. It would seem, from this formation, that ethyldibenzil is really a derivative of benzilic acid.