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THE ALKALINE CLEAVAGE OF 4-NITROBENZIL AND 3,3′-DINITROBENZIL

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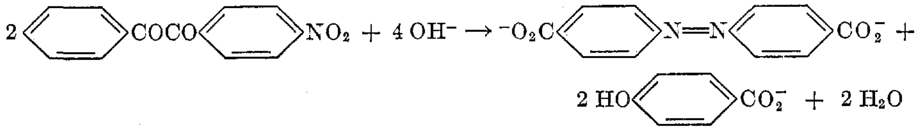
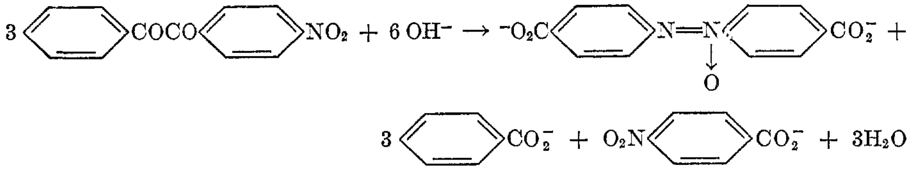
In connection with a study of the influence of substituents on the rates of base-catalyzed rearrangement of benzils, it was found that 4-nitrobenzil and 3,3′-dinitrobenzil underwent cleavage instead of rearrangement to the benzilic acids. The cleavage of the 4-nitro compound had been observed by Zinin (1) who, on the basis of certain analytical evidence, regarded the reaction products to be azobenzene-4,4′-dicarboxylic and 4-hydroxybenzoic acids, formed by the reaction:



1.

It was readily confirmed that more than one mole of base per mole of benzil was rapidly consumed, wheras normal rearrangement or cleavage to an aldehyde and acid would require only one mole of base per mole of benzil. However, none of the azobenzene-4,4′-dicarboxylic nor 4-hydroxybenzoic acids could be obtained, but a good yield of azoxybenzene-4,4′-dicarboxylic acid was isolated. This may be formed according to the reaction:



2.

Benzoic acid was isolated, though not in the quantities required by reaction 2. Decomposition during the isolation process of sublimation plus the presence of a small quantity of unidentified by-product may well account for the low yield. The fact that the azoxy compound was found in quantities in excess of those predicted by the above equation while little nitrobenzoic acid could be detected, indicated that much of the latter had undergone reductive coupling, either with itself or with unreacted benzil, to form additional azoxybenzene-4,4′-dicarboxylic acid.

Klinger and Martinoff (2) found that alkali metal hydroxides react with 3,3′-dinitrobenzil to give an insoluble metal salt, presumably that of the benzilic acid, but that acidification of a solution of the salt resulted in the formation of a tar. They found that when barium hydroxide was used, and the procedure re-

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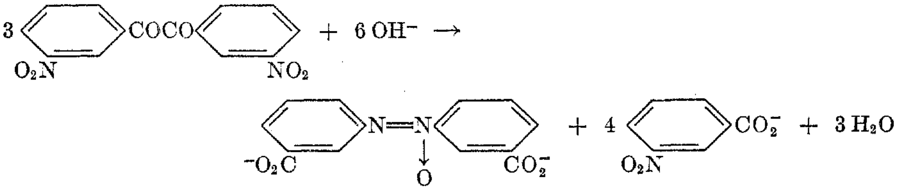
peated, isolable quantities of 3-nitrobenzoic acid were obtained. Other products were not identified.

In this research, similar results were obtained when the work of Klinger and Martinoff (2) was repeated. When the benzil was treated with a solution of "Triton B" (trimethylbenzylammonium hydroxide) only 3-nitrobenzoic acid and tars could be obtained. However, when the benzil was allowed to react with aqueous sodium hydroxide for a few seconds only, and the mixture quickly poured into acetic acid, azoxybenzene-3,3′-dicarboxylic acid was isolated. Quantitative studies indicated the following reactions:



3.

Here the 3-nitrobenzoic acid does not undergo reductive coupling to form additional azoxy compounds, probably on account of the short contact time.

The similarity in the reactions of the 3-nitro and 4-nitro compounds makes it difficult to postulate for the formation of the azoxy compound a mechanism based on tautomeric effects.

EXPERIMENTAL

(*a*). *Preparation of 4-nitrobenzil.* The method of Womack, Campbell, and Dodds (3) was used to prepare 4′-nitrobenzoin acetate by the nitration of benzoin in acetic anhydride-sulfuric acid solution. Three treatments of a 95% ethanol solution of the product with activated charcoal, and recrystallization after each treatment gave 28% of purified material which melted at 124.5–125°. Oxidative hydrolysis of this compound gave the 4-nitrobenzil, 77.7% yield (based on the acetate). Activated charcoal treatments and crystallization from 95% ethanol, aqueous acetone, glacial acetic acid, aqueous acetone, and 95% ethanol gave a canary-yellow crystalline solid which melted at 139.5–140.0°.

Anal. Calc'd for $C_{14}H_9NO_4$: N, 5.48. Found: N, 5.39.

(*b*). *Preparation of 3,3′-dinitrobenzil.*[2] This compound was prepared by the method of Klinger and Martinoff (2). After two recrystallizations from aqueous ethanol, the pale yellow, crystalline diketone melted at 108.5–109°.

(*c*). *Preparation of reference samples of azoxybenzenedicarboxylic acids, and their esters.* Reductive coupling of *p*-nitrobenzoic acid (4) with arsenite gave azoxybenzene-4,4′-dicarboxylic acid in almost quantitative yield. The acid was converted to its dimethyl and diethyl esters by refluxing for three days a suspension of 10–15 g. of the acid in 200 ml. of the anhydrous alcohol to which had been added 20–30 ml. of conc'd sulfuric acid. The diethyl ester was recrystallized from 95% ethanol and the dimethyl ester from aqueous acetone. Azoxybenzene-3,3′-dicarboxylic acid and its dimethyl ester were prepared using *m*-nitrobenzoic acid and the method just described.

(*d*). *Cleavage of 4-nitrobenzil.* 4-Nitrobenzil (25.76 g., 0.101 mole) was dissolved by warming in 1235 ml. of 90% by volume aqueous ethanol. A solution of 11.58 g. of potassium hydroxide in 232 ml. of 90% ethanol was rapidly stirred into the benzil solution. The solution was stirred and heated (maximum temperature 78°) for one hour and then chilled in an ice-bath. Both the solid which separated, and the solution were worked up by methods of

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[2] The authors are indebted to Dr. Comer D. Shacklett who prepared the 3,3′-dinitrobenzil.

extraction, recrystallization, and sublimation to yield the following: 0.42 g. of recovered 4-nitrobenzil; 17.95 g. of azoxybenzene-4,4′-dicarboxylic acid; 5.30 g. of a mixture of benzoic and *p*-nitrobenzoic acids; and 0.3 g. of unidentified solids. The recovered 4-nitrobenzil was identified by melting point and mixture melting point with the starting material. The azoxybenzene-4,4′-dicarboxylic acid has no characteristic melting point. It was converted to its methyl and ethyl esters for analysis and comparison with authentic samples. The results were as follows: *Dimethyl ester*, m.p. 205–206.5°; m.p. of authentic sample 205.2–206.2°; mixture m.p. 204.8–205.5°:

Anal. Calc'd for $C_{14}H_{14}N_2O_5$: C, 61.14; H, 4.49.
Found: C, 61.77; H, 4.38.

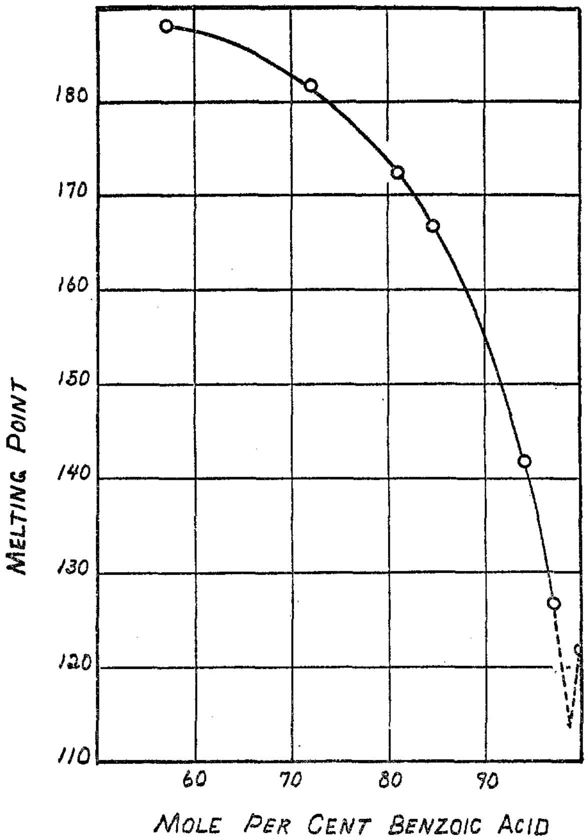

FIG. 1. MELTING POINT DIAGRAM FOR THE SYSTEM BENZOIC ACID-NITROBENZOIC ACID

Diethyl ester: transition point 114.5°, m.p. 121.5°; for an authentic sample, transition point 114.5°; m.p. 120.5–121.2°; mixture transition point, 114–114.4°; mixture m.p. 120.8–121.2°.

Anal. Calc'd for $C_{16}H_{16}N_2O_5$: C, 63.14; H, 5.30.
Found: C, 63.27; H, 5.22.

Samples of benzoic and nitrobenzoic acids were obtained from their mixture by fractional sublimation and were identified by melting point and mixture melting point with authentic samples. The analysis of the mixture was made from its melting point. Determination of the melting points of standard mixtures of the two acids gave the simple eutectic melting point diagram shown in Figure 1. A melting point of 128–129° for the mixture from the cleavage experiments indicated 95.5 mole-% benzoic acid and 4.5 mole-% nitrobenzoic acid. The amount of alkali consumed during the cleavage process was determined by titration procedures.

Table I gives a comparison of the experimental quantities and those required by equation 2, assuming that all of the nitrobenzoic acid has undergone reductive coupling.

(*e*). *Cleavage of 3,3'-dinitrobenzil.* A suspension of 9.253 g. (0.0308 mole) of 3,3'dinitrobenzil, 7.48 g. of barium hydroxide, and 134 ml. of water was refluxed for two hours. The mixture was cooled, and the solid removed by filtration. A solution of the solid was acidified; the products obtained were 4.01 g. of 3-nitrobenzoic acid and 3.07 g. of an unidentified brown tar.

The benzil (50 g., 0.167 mole) was added to 139.2 ml. of 40% aqueous "Triton B" (trimethylbenzylammonium hydroxide) and 150 ml. of cold water. The addition required about 30 minutes. After one hour at room temperature the reaction mixture was stirred into 42.7 ml. of concentrated hydrochloric acid in 500 ml. of cold water. Attempts to work up the cleavage product led to the isolation of 23.16 g. (0.139 mole) of 3-nitrobenzoic acid, identified by melting point and mixture melting point with an authentic sample. Unidentified tarry materials were also formed.

TABLE I

SUMMARY OF RESULTS OBTAINED FROM THE MATERIAL BALANCE ON THE CLEAVAGE OF 4-NITROBENZIL

REACTANT OR PRODUCT	MOLAR RATIO	
	Calculated	Found
4-Nitrobenzil	0.50	0.42
Base	1.00	1.00
Azoxybenzene-4,4'-dicarboxylic acid	.25	.27
Benzoic acid	.50	.15
4-Nitrobenzoic acid	.00	.02

TABLE II

SUMMARY OF RESULTS OBTAINED FROM THE MATERIAL BALANCE ON THE CLEAVAGE OF 3,3'-NITROBENZIL

REACTANT OR PRODUCT	MOLAR RATIO	
	Calculated	Found
3,3'-Dinitrobenzil	3	2.91
Sodium hydroxide[a]	6	6.00
Azoxybenzene-3,3'-dicarboxylic acid	1	0.86
m-Nitrobenzoic acid	4	3.45

[a] Determined by titration with standard acid of the excess sodium hydroxide remaining after reaction with 2 g. of benzil.

Solutions of 20 g. (0.067 mole) of 3,3'-dinitrobenzil in 100 ml. of dioxane, and of 250 ml. of normal aqueous sodium hydroxide were brought to the boiling temperature, very quickly mixed (violent boiling), and immediately quenched by pouring into 250 ml. of normal acetic acid.[3] The contact time did not exceed five seconds. The reaction mixture was extracted with

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[3] This procedure was suggested by Mr. Leonard Doub. The authors are grateful for his interest in the work.

ether, the extract dried over magnesium sulfate, and the solvent evaporated. The residue was treated three times with hot water and cooled to yield 3.84 g. of 3-nitrobenzoic acid, identified by melting point and mixture melting point with an authentic sample. The residue was subjected to fractional crystallization (six times from hot aqueous ethanol) to yield 13.52 g. of 3,3′-dinitrobenzil which gave no melting point depression when mixed with the starting benzil, plus 1.69 g. of azoxybenzene-3,3′-dicarboxylic acid. The neutral equivalent of the latter compound was 141.7 (Calc'd 143.0). It was converted to the dimethyl ester which melted at 133–134.5° and showed no depression when mixed with an authentic sample. Table II shows the agreement between experiment and theory as required by equation 3.

SUMMARY

The alkaline cleavages of 4-nitrobenzil and 3,3′-dinitrobenzil have been studied. It has been demonstrated that the azoxybenzenedicarboxylic acids plus benzoic and nitrobenzoic acids are formed. The reactions have been studied quantitatively, and equations for the reactions have been formulated.

KNOXVILLE, TENNESSEE

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(2) KLINGER AND MARTINOFF, *Ann.*, **389**, 232 (1912).
(3) WOMACK, CAMPBELL, AND DODDS, *J. Chem. Soc.*, 1402 (1938).
(4) MEYER AND DAHLEM, *Ann.*, **326**, 331 (1903).