Conclusions.

The copepods and schizopods (shrimp) constitute the chief forms of feed of the small sea herring of the Passamaquoddy Bay region. Of the copepods *Calanus finmarchicus*, *Pseudocalanus elongatus*, and *Temora longicornis* appear to be the chief species found in this region, and may be classed as the "red feed," as distinguished from shrimp.

The results of the examinations made show that ammonia and amines are found in very appreciable quantities when the different forms of food decompose. These results also show with what rapidity and to what extent the food decomposed. When the 2 kinds of bacteria, so commonly found associated with the feed, are grown in pure culture it is shown that ammonia and amines are formed in the media.

Skatole and indole were also detected in the culture media on which these bacteria were grown. Ammonia and amines were also determined in the contents of the digestive tract of "belly-blown," feedy fish. The results show that the formation of ammonia and amines in the decomposing food is due to the action of the 2 bacteria always found asssociated with the 2 forms of food (copepods and schizopods), whether taken directly from the water or from the digestive tracts of the fish. This decomposition, also accompanied by the evolution of gas when *Bacillus B* is present, is responsible for the bursting of the bellies ("belly-blown") of "feedy" fish.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

SOME DERIVATIVES OF 2,4-DINITRO-BENZALDEHYDE.[1]

BY ALEXANDER LOWY AND BLAINE B. WESCOTT.

Received February 11, 1920.

The work upon the derivatives of 2,4-dinitro-benzaldehyde was undertaken for the following reasons: (1) Upon examination, the literature revealed that relatively few derivatives of this compound have been prepared.[2] (2) Research upon trinitro-benzaldehyde was already under way in these laboratories and the results of this work, to be published in the near future, showed the desirability of a parallel investigation upon 2,4-dinitro-benzaldehyde. (3) Since benzaldehyde has long been an important intermediate in the dye industry it seemed probable, reasoning by analogy, that 2,4-dinitro-benzaldehyde might also find considerable use in the manufacture of dyestuffs. (4) But perhaps the most im-

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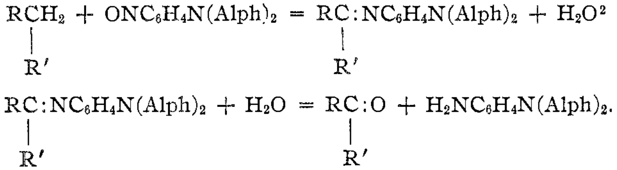
[1] This report represents a part of a thesis presented by Blaine B. Wescott in partial fulfillment of the requirements for the degree of Master of Science, January, 1920.

[2] *Ber.*, **35**, 1224 (1902); *ibid.*, **35**, 2704 (1902); *Monatsh.*, **23**, 1003 (1902); *Ber.*, **37**, 1861 (1904); *ibid.*, **39**, 2754 (1906); *ibid.*, **40**, 3230 (1907); *Monatsh.*, **23**, 554 (1902); *Ber.*, **41**, 109 (1908); *ibid.*, **42**, 601 (1909); *J. prakt. Chem.*, **2**, 89.

portant reason for the research upon this compound is the fact that it is a derivative of 2,4-dinitro-toluene, an important explosive, which is itself an intermediate in the manufacture of trinitro-toluene. It is evident that an outlet for the great stocks of 2,4-dinitro-toluene and trinitro-toluene now on hand is an economic necessity. Such an outlet was suggested in 2,4-dinitro-benzaldehyde and trinitro-benzaldehyde. The method used in the preparation of 2,4-dinitro-benzaldehyde was essentially that described by F. Sachs and R. Kempf.[1] They stated that the conversion of the methyl group of an aromatic compound to the aldehyde group is possible by a condensation with a nitroso-dialkyl-aniline and subsequent hydrolysis with mineral acids.



$$\underset{\mathrm{R'}}{\underset{|}{\mathrm{RCH_2}}} + \mathrm{ONC_6H_4N(Alph)_2} = \underset{\mathrm{R'}}{\underset{|}{\mathrm{RC{:}NC_6H_4N(Alph)_2}}} + \mathrm{H_2O}\ [2]$$

$$\underset{\mathrm{R'}}{\underset{|}{\mathrm{RC{:}NC_6H_4N(Alph)_2}}} + \mathrm{H_2O} = \underset{\mathrm{R'}}{\underset{|}{\mathrm{RC{:}O}}} + \mathrm{H_2NC_6H_4N(Alph)_2}.$$

They found that the above reactions proceeded easily in the preparation of 2,4-dinitro-benzaldehyde and they described the following method for its production. 45 g. of 2,4-dinitro-toluene, 40 g. of nitroso-dimethyl-aniline, 75 g. of sodium carbonate (anhydrous crystals) and 250 cc. of 95% ethyl alcohol were heated together on a steam bath for 5 hours under a reflux condenser, with frequent shaking. After a time nearly the whole mixture solidified to a mass of green granules. After filtration, the residue was washed with several liters of hot water. The yield of the condensation product was 86%. The condensation product was then shaken with 250 cc. of 27% nitric acid and 250 cc. of benzene for some hours. The mixture was filtered and the benzene layer separated from the filtrate. After the benzene had been distilled, the residue, a dark oil which solidified on cooling, was dissolved in alcohol and boiled with animal charcoal. The charcoal was then filtered off and just enough water added to the filtrate to cause it to become cloudy. The aldehyde crystallized out upon standing in long, yellow needles which melted at 72°. Yield, 88%. Several difficulties were encountered at once in their process wnich necessitated considerable investigation. (1) A low yield, 25%, of the product was obtained. (2) Considerable quantities of oil adhered to the crystals. (3) 250 cc. of benzene was found to be an entirely inadequate amount for the complete extraction of the 2,4-dinitro-benzaldehyde.

The reactions carried out in the study of 2,4-dinitro-benzaldehyde were all of the general type known as condensations. The first type of condensation studied was that of the reaction between 2,4-dinitro-benzaldehyde

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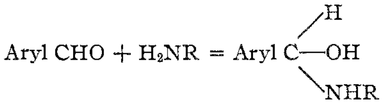
[1] *Ber.*, 35, 2704 (1902).

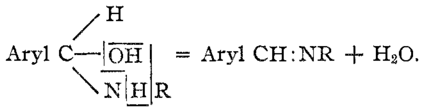
[2] *Ibid.*, 32, 2341 (1899); 33, 959 (1900); 34, 118, 498 (1901); 34, 3047 (1901).

and different aromatic amines. The reaction is accompanied by the elimination of one molecule of water and may be expressed by the general type reaction, Aryl CHO + H_2NR = Aryl CH:NR + H_2O. The class of condensation products formed in reactions as typified by the above equation are known as "Schiff's bases."[1] The reaction proceeds in 2 stages: The first consists of the formation of an intermediate addition product,

1. 

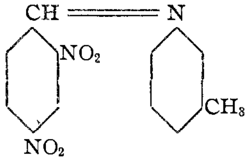
$$\text{Aryl CHO} + \text{H}_2\text{NR} = \text{Aryl C}\begin{array}{l}\diagup\text{H}\\ \text{—OH}\\ \diagdown\text{NHR}\end{array}$$

The second consists of the splitting off of one molecule of water from the addition product,

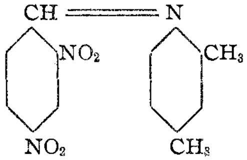
2. 

$$\text{Aryl C}\begin{array}{l}\diagup\text{H}\\ \text{—}\boxed{\text{OH}}\\ \diagdown\text{N}\boxed{\text{H}}\text{R}\end{array} = \text{Aryl CH:NR} + \text{H}_2\text{O}.$$

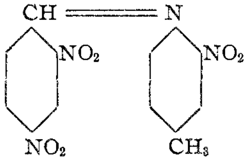
The same type of reaction is possible with either substituted aldehydes or amines or both. Condensations were carried out between 2,4-dinitrobenzaldehyde and various substituted amines giving the following products:



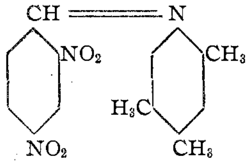
(I).



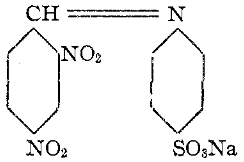
(II).



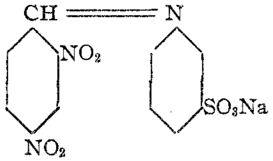
(III).



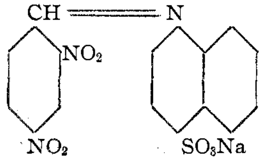
(IV).



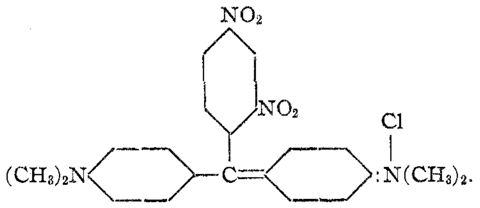
(V).



(VI).



(VII).



(VIII).

It is often impossible to isolate the intermediate addition product of the aldehyde-amine condensations due either to the instability of the compound or to the velocity of the second stage of the reaction. Although the isolation of the addition product in the condensation of 2,4-dinitro-

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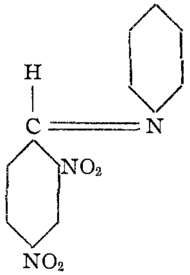
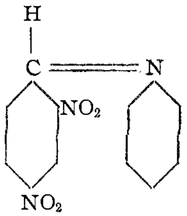
[1] *Ber.*, 35, 984 (1902).

benzaldehyde and aniline was attempted, the effort was not successful. More work upon this phase of the subject is to be undertaken at a later date.

The results of the work proceeding simultaneously upon trinitrobenzaldehyde, which will be published in the near future, suggested the possibility of the existence of the condensation products in 2 stereoisomeric forms. The 2 stereoisomeric forms of the 2,4-dinitro-benzylidine-aniline would be represented by the following formulas:



syn type.



anti type.

However, no evidence of the existence of 2 stereoisomeric forms of any of the condensation products produced from 2,4-dinitro-benzaldehyde was found.

The second type of condensation studied was that taking place in the reaction of one molecule of an aromatic aldehyde and 2 molecules of a tertiary alkylaniline in the presence of a condensing agent such as anhydrous zinc chloride, or conc. hydrochloric acid. This type of condensation was used to obtain 2,4-dinitro-tetramethyl-diamino-triphenyl-methane. The reactions were analogous to those used to produce malachite green. The experiments were of a qualitative nature only but the quantitative results are to be worked out and published in a later paper. The dye as prepared in the preliminary trials dyed silk a greenish blue shade, very much like that produced by malachite green.

Experimental Part.

Preparation of 2,4-Dinitro-benzaldehyde.—The following method for the preparation of 2,4-dinitro-benzaldehyde was finally adopted after considerable investigation. 100 g. of 2,4-dinitrotoluene, 89 g. of nitrosodimethylaniline, 167 g. of sodium carbonate and 555 cc. of alcohol were heated for 5 hours on a steam bath under a reflux condenser. The condensation product was filtered free of alcohol and leached with acetic acid until the sodium carbonate was entirely decomposed, after which the mixture was filtered and the residue washed free of acetic acid with water. The condensation product was hydrolyzed by treatment with 250 cc. of 1:1 hydrochloric acid for 3 hours at 80° with mechanical stirring. The resulting mixture was extracted repeatedly with hot benzene. The small amount of oily material from the acid layer which passed over into the benzene extract was removed by filtration. The benzene was then distilled off and the 2,4-dinitro-benzaldehyde recovered from the residue by repeated extraction with hot water. The water extract was separated from the oil by filtration through a hot-water funnel. The 2,4-dinitrobenzaldehyde separated from the filtrate in long, yellow needles upon cooling. The melting point of the 2,4-dinitro-benzaldehyde obtained by the above process was 71°. The identity of the product was further established by carrying out the condensation with aniline as described by Sachs and Kempf.[1]

2,4-Dinitrobenzal-*m*-toluidine, $C_6H_3(NO_2)_2CH:NC_6H_4(CH_3)$ (I).—This compound was prepared by adding 2.8 g. of *m*-toluidine to 5 g. of 2,4-dinitro-benzaldehyde dissolved in 25 cc. of glacial acetic acid. The condensation product separated almost immediately. The mixture was heated on a steam bath to insure the completion of the reaction. After 2 hours it was cooled, diluted with water, filtered and washed with dil. acetic acid and water. The product was purified by recrystallization from benzene. The purified substance crystallized in fine, yellow needles which melted at 130°. It was easily soluble in benzene, chloroform, acetic acid and acetone, slightly soluble in alcohol, and insoluble in water. Yield, 5.4 g. The product gave 2,4-dinitro-benzaldehyde upon hydrolysis with hot 1 : 1 hydrochloric acid.

Subs., 0.2000, 0.2050; 26.55 cc. N (18.0°, 742 mm.), 27.3 cc. N (20.5°, 744.5 mm.).
Calc. for $C_6H_3(NO_2)_2CH:NC_6H_4(CH_3)$: N, 14.73. Found: 14.89, 14.79.

2,4-Dinitrobenzal-1,3,4-xylidine, $C_6H_3(NO_2)_2CH:NC_6H_3(CH_3)_2$ (II).—This substance was prepared by adding 3 g. of 1,3,4-xylidine to 5 g. of 2,4-dinitro-benzaldehyde dissolved in 25 cc. of glacial acetic acid after which the mixture was heated for 2 hours on a steam bath. It was then cooled, diluted with water, filtered and washed with dil. acetic acid and water. The product was purified by recrystallization from acetone. It formed long, deep yellow needles of a silky luster having a melting point of 210.5°. The compound is fairly soluble in benzene, acetone, chloroform and acetic acid, slightly soluble in alcohol and insoluble in water. Yield, 7 g. Upon hydrolysis with hot 1 : 1 hydrochloric acid it yielded 2,4-dinitro-benzaldehyde.

Subs., 0.2018, 0.2014, 0.2004; 25.38 cc. N (17.0°, 731.6 mm.), 25.7 cc. N (20.0°, 747.6 mm.), 25.9 cc. N (22.0°, 742 mm.).
Calc. for $C_6H_3(NO_2)_2CH:NC_6H_3(CH_3)_2$: N, 14.04. Found: 13.97, 14.27, 14.21.

2,4-Dinitrobenzal-3-nitro-4-toluidine, $C_6H_3(NO_2)_2CH:NC_6H_3(NO_2)(CH_3)$ (III).—A solution of 4 g. of 3-nitro-4-toluidine in 50 cc. of glacial acetic acid was added to a solution of 5 g. of 2,4-dinitro-benzaldehyde in 50 cc. of glacial acetic acid. The mixture was heated for 2 hours on a steam

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[1] *Ber.*, 35, 1224 (1902).

bath after which it was evaporated until crystallization took place. Purification was accomplished by recrystallization from glacial acetic acid. The substance separated in radiating clusters of fine, light brownish yellow needles which had a melting point of 195°. The product was easily soluble in acetone, chloroform and glacial acetic acid, slightly soluble in alcohol and benzene and very slightly soluble in water. Yield, 3.2 g. Upon hydrolysis with hot 1 : 1 hydrochloric acid it yielded 2,4-dinitro-benzaldehyde.

Subs., 0.2008, 0.1196; 30.3 cc. N (19.5°, 739.7 mm.), 19 cc. N (23.5°, 731.8 mm.).

Calc. for $C_6H_3(NO_2)_2CH:NC_6H_3(NO_2)(CH_3)$: N, 16.96. Found: 16.75, 17.09.

2,4 - Dinitrobenzal - pseudocumidine, $C_6H_3(NO_2)_2CH:NC_6H_2(CH_3)_3$: (IV).—This substance was prepared by adding a solution of 2.3 g. of pseudocumidine dissolved in 25 cc. of glacial acetic acid to a solution of 3.4 g. of 2,4-dinitro-benzaldehyde dissolved in 75 cc. of glacial acetic acid. The condensation product separated immediately in a bright yellow mass. The mixture was heated for 2 hours on a steam bath after which it was diluted with water, filtered, washed with dil. acetic acid and water. The product was purified by recrystallization from benzene from which it separated in fine, bright yellow needles with a silky luster. The melting point of the compound was 186.5°. Yield, 4.4 g. The product was easily soluble in benzene, acetone, chloroform and acetic acid, slightly soluble in alcohol and ether, and insoluble in water. Upon hydrolysis with hot 1:1 hydrochloric acid it gave 2,4-dinitro-benzaldehyde.

Subs., 0.2022, 0.2017, 0.2018; 24.98 cc. N (19.0°, 733 mm.), 24.95 cc. N (20.0°, 735 mm.), 25.5 cc. N (22.0°, 730.7 mm.).

Calc. for $C_6H_3(NO_2)_2CH : NC_6H_2(CH_3)_3$: N, 13.42. Found: 13.62, 13.61, 13.68.

2,4-Dinitrobenzal-sodium Sulfanilate, $C_6H_3(NO_2)_2CH:NC_6H_4SO_3Na.H_2O$ (V).—This product was prepared by adding 5 g. of 2,4-dinitrobenzaldehyde dissolved in 50 cc. of alcohol to 5 g. of sodium sulfanilate dissolved in 150 cc. of alcohol. The mixture was heated for 2 hours on a steam bath under a reflux condenser after which it was evaporated to crystallization. The mother liquor was filtered off and a further evaporation yielded more of the product. The compound was purified by recrystallization from 1:1 alcohol. It separated in very fine, pale yellow crystals, which decomposed at 249°. The product was easily soluble in water, and slightly soluble in alcohol, ether, benzene, acetone and chloroform. Yield, 8.2 g. Upon hydrolysis with hot 1:1 hydrochloric acid it gave 2,4-dinitro-benzaldehyde. The water of crystallization was determined by heating the air-dry product for 12 hours at 105°.

Subs. (air dry), 0.2120, 0.2930; loss, 0.0098, 0.0132 (12 hours at 105°).

Calc. for $C_{13}H_8N_3O_7SNa.H_2O$, 4.60. Found: 4.62, 4.50.

Subs., 0.1683; $BaSO_4$, 0.0999.

Calc. for $C_{13}H_8N_3O_7SNa.H_2O$: S, 8.20. Found: 8.15.

Subs., 0.2019, 0.2007; 19.5 cc. N (17.5°, 733 mm.), 19.85 cc. N (17.5°, 732.2 mm.).

Calc. for $C_{13}H_8N_3O_7SNa.H_2O$: N, 10.73. Found: 10.73, 10.96.

2,4-Dinitrobenzal-sodium Metanilate, $C_6H_3(NO_2)_2CH:NC_6H_4SO_3Na.3H_2O$ (VI).—This compound was made by adding 5 g. of 2,4-dinitrobenzaldehyde dissolved in 50 cc. of alcohol to 5 g. of sodium metanilate dissolved in 250 cc. of alcohol. After $^3/_4$ of the alcohol had been evaporated the mixture was heated for 2 hours on a steam bath under a reflux condenser. It was evaporated to crystallization and a further amount of the product recovered from the mother liquor after filtration and further evaporation of the filtrate. The compound was purified by recrystallization from 1:1 alcohol from which it separated in very fine, deep yellow needles. The product decomposed at 185°. Yield, 5.4 g. The substance was soluble in water and slightly soluble in alcohol, chloroform, acetone and benzene. The water of crystallization was determined by heating the air-dry product for 12 hours at 105°.

Subs. (air-dry), 0.4617, 0.1896, 0.1514; loss, 0.0613, 0.0252, 0.0199 (12 hours at 105°).

Calc. for $C_{13}H_8N_3O_7SNa.3H_2O$: H_2O, 12.65. Found: 13.28, 13.29, 13.14.

Subs. (dry), 0.2013, 0.2003; 21.8 cc. N (24.0°, 739.2 mm.), 21.9 cc. N (26.5°, 734.8 mm.).

Calc. for $C_{13}H_8N_3O_7SNa.3H_2O$: N, 9.83. Found: 10.24, 10.14.

Subs. (dry), 0.2049; $BaSO_4$, 0.1270.

Calc. for $C_{13}H_8N_3O_7SNa.3H_2O$: S, 7.50. Found: 7.43.

2,4-Dinitrobenzal-sodium Naphthionate, $C_6H_3(NO_2)_2CH:NC_{10}H_6SO_3Na.0.5H_2O$ (VII).—This substance was prepared by adding 5 g. of 2,4-dinitro-benzaldehyde dissolved in 50 cc. of alcohol to 6.3 g. of sodium naphthionate dissolved in 180 cc. of alcohol. After $^1/_4$ of the alcohol had been evaporated the mixture was heated for 2 hours on a steam bath under a reflux condenser. The product was obtained by the evaporation of the solution to crystallization. A further quantity was recovered by the evaporation of the mother liquor after filtration. The substance was purified by recrystallization from 1:1 alcohol from which it separated in very fine, bright orange needles which decomposed at 248°. Yield, 7.9 g. It was soluble in water and slightly soluble in alcohol, ether, benzene, chloroform and acetone. It yielded 2,4-dinitro-benzaldehyde upon hydrolysis with hot 1:1 hydrochloric acid. The water of crystallization was found by heating the air-dry product for 12 hours at 105°.

Subs. (air-dry), 0.3144, 0.1032; loss, 0.0062, 0.0018 (12 hours at 105°).

Calc. for $C_{17}H_{10}N_3O_7SNa.0.5H_2O$: H_2O, 2.08. Found: 1.97, 1.79.

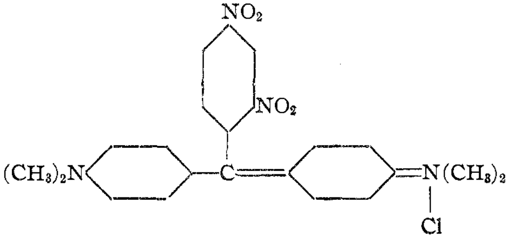
Subs. (dry), 0.1318; $BaSO_4$, 0.0762.

Calc. for $C_{17}H_{10}N_3O_7SNa.0.5H_2O$: S, 7.42. Found: 7.76.

Subs., 0.2014, 0.2006; 18.6 cc. N (24.0°, 726 mm.), 17.65 cc. N)17.0°, 745.2 mm.).

Calc. for $C_{17}H_{10}N_3O_7SNa.0.5H_2O$: N, 9.72. Found: 9.82, 9.95.

2,4 - Dinitro - benzaldehyde - dimethylaniline Condensation. VIII.—This condensation which is analogous to that carried out in the preparation of malachite green was performed only in a qualitative way. The directions given for the preparation of malachite green by Gattermann[1] were followed. The product obtained was a green powder which dyed silk a bluish green shade very similar to that produced by malachite green. The following formula undoubtedly represents the structure of the dye:



The quantitative results, as stated above, will be published in a later paper.

Summary.

1. The method described by Sachs and Kempf for the preparation of 2,4-dinitro-benzaldehyde was found to be unsatisfactory and a modified method for its preparation was worked out.

2. Eight derivatives of 2,4-dinitro-benzaldehyde were prepared and analyzed and certain physical properties and solubilities determined.

3. These compounds, like many other similar condensation products, are affected to a greater or less extent by the action of light.

PITTSBURGH, PENNA.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY. No. 85.]

A STUDY OF THE SULFUR DERIVATIVES OF BUTYL ALCOHOL.

BY H. LEB. GRAY AND GURNEY O. GUTEKUNST.

Received February 20, 1920.

In the course of our work in this laboratory, it was necessary to prepare large quantities of butyl sulfone. This involved not only a complete study of the methods of preparation of the sulfone but of butyl sulfide as well.

Grabowsky and Saytzeff[2] prepared butyl sulfide by heating an alcoholic solution of potassium sulfide with butyl iodide. A disadvantage of this method consists in the difficulty of preparing large quantities of alcoholic sodium or potassium sulfide so it was decided to prepare the butyl sulfide by distilling sodium sulfide with an aqueous solution of sodium butyl sulfate, the latter being prepared by the action of fuming sulfuric acid on butyl alcohol.

It was found that low yields were obtained by this method; this was

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[1] "Practical Methods of Organic Chemistry."

[2] *Ann.*, 171, 251 (1874).