

	Found	Calculated
K.....	3.85	4.22
NH ₄	9.79	9.72
Mg.....	8.43	7.87
Fe.....	17.96	18.06
H ₂ O.....	9.94	9.70

Experiment indicates that cadmium¹ forms compounds of a similar composition. The investigation of these products is being continued in this laboratory.

WASHBURN COLLEGE,
Topeka, Kan., Feb. 16, 1907.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA
UNIVERSITY, No. 132.]

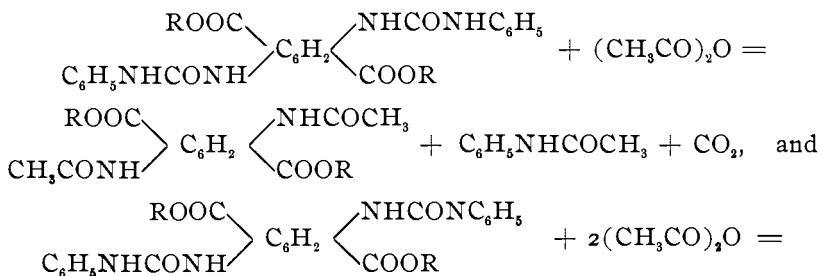
RESEARCHES ON QUINAZOLINES (19TH PAPER). THE SYNTHESIS OF 1,3,6,8-NAPHTHOTETRAZINES FROM PARADIAMINOTEREPHTHALIC ACID AND FROM CERTAIN OF ITS DERIVATIVES.²

BY MARSTON TAYLOR BOGERT AND JOHN MAURICE NELSON.

Received February 9, 1907.

Bogert and Dox prepared two naphthotetrazines from ethyl succinylsuccinate, one by condensation with guanidine³, the other by condensation with acetamidine⁴. Their attempts to obtain similar compounds from *p*-diaminoterephthalic acid resulted unsuccessfully. The authors of the present paper, as the result of further experimenting in this direction, have now succeeded in accomplishing this synthesis, and have prepared and studied several naphthotetrazines from *p*-diaminoterephthalic compounds. The experiments may be briefly summarized as follows:—

When ethyl *p*-diaminoterephthalate is treated with phenyl isocyanate, ethyl diphenyluraminoterephthalate results. By the action of acetic anhydride upon this phenyluramino ester, ethyl *s*-diacetyldiaminoterephthalate, and tetracetyldiaminoterephthalate are formed, according to the following equations:

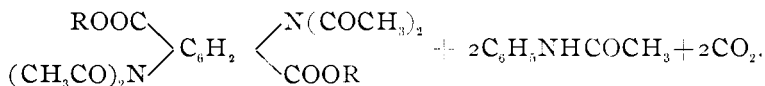


¹ This has the composition K₂CdFe(CN)₆, 4(NH₄)₂CdFe(CN)₆·2H₂O.

² Read at the Meeting of the New York Section, February 8, 1907.

³ This Journal, 27, 1127 (1905).

⁴ Ibid., 27, 1302 (1905).



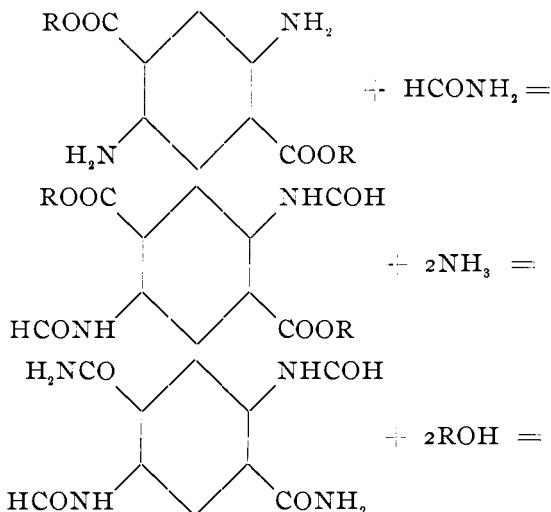
It is worth noting that the tetracetyldiaminoterephthalate was easily obtained by this reaction, whereas only the diacetyldiamino derivative was formed by the action of acetic anhydride upon ethyl *p*-diaminoterephthalate itself. This suggests the possibility that other primary amines which yield only monacetyl derivatives by direct acetylation may be converted into diacetyl derivatives through the phenyluramino compound. We shall test this question later, as time permits.

From *p*-diaminoterephthalic acid and acetic anhydride, the di-acetan-thranil (di-lactam of *s*-diacetyl-*p*-diaminoterephthalic acid) was obtained:



Naphthotetrazines were prepared by heating ethyl *p*-diaminoterephthalate with formamide¹, by heating its acetyl derivative with primary amines², by the action of primary amines upon the above di-acetan-thranil³, and by heating the diphenyluraminoterephthalic ester with aniline; the reactions involved being as follows:

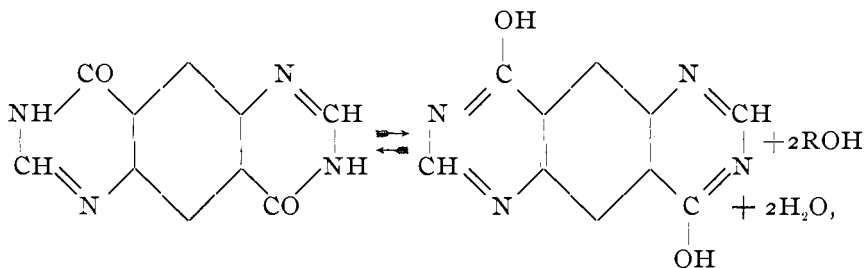
I.



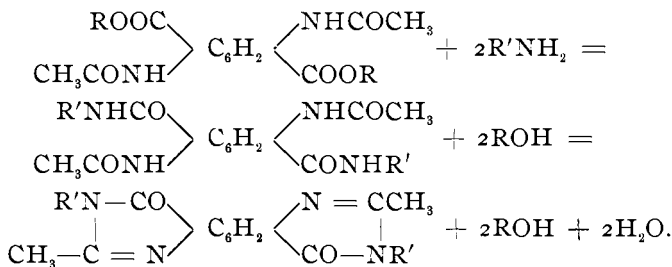
¹ Niementowski, J. pr. Chem., 51, 564 (1895); Bogert and Chambers, This Journal, 27, 650 (1905).

² Weddige, J. pr. Chem., 36, 141 (1887); Zacharias, Ibid., 43, 432 (1891); Thieme, Ibid., 43, 451 (1891).

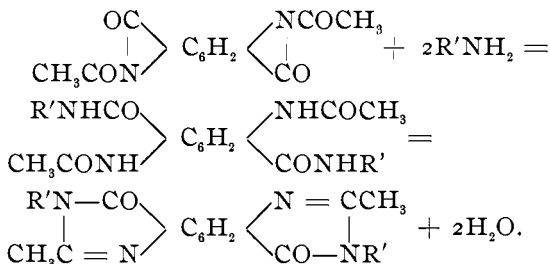
³ Anschütz, Schmidt and Greiffenberg, Ber., 35, 3840 (1902); Bogert and Chambers, This Journal, 27, 649 (1905), 28, 207 (1906); Bogert and Seil, Ibid., 27, 1305 (1905), 28, 884 (1906).



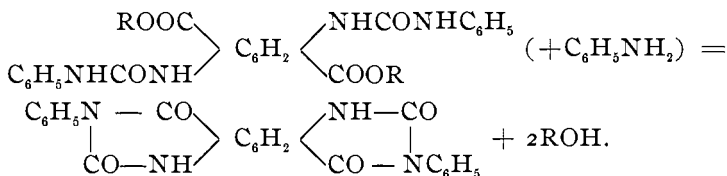
II.



III.



IV.



By these various reactions, the following naphthotetraazines were prepared: 4,9-diketotetrahydro-1,3,6,8-naphthotetraazine (4,9-dihydroxy-1,3,6,8-naphthotetraazine), the 2,7-dimethyl derivative of the latter, 2,7-dimethyl-3,8-diisoamyl-4,9-diketotetrahydro-1,3,6,8-naphthotetraazine (and the corresponding intermediate amide), 2,7-dimethyl-3,8-diphenyl-4,9-diketotetrahydro-1,3,6,8-naphthotetraazine, and 3,8-diphenyl-2,4,7,9-tetraketo-octahydro-1,3,6,8-naphthotetraazine (3,8-diphenyl-2,7-dihydroxy-4,9-diketotetrahydro-1,3,6,8-naphthotetraazine). Most of these substances melt very high or are infusible. They are insoluble or very difficultly soluble in the usual organic solvents. The isoamyl compound, however, melts relatively low (179° corr.), and can be crystallized from

alcohol. We have pointed out elsewhere that in the 4-quinazolones as the molecular weight of the alkyl increases the melting point falls, and it is not unlikely that the same will be found to be the case with these naphthotetrazines. Of the naphthotetrazines investigated so far, those containing the group $-\text{CONH}- \rightleftharpoons -\text{C}(\text{OH}):\text{N}-$ dissolve readily in dilute caustic alkalies, and are re-precipitated from such solutions by dilute acids or by carbon dioxide.

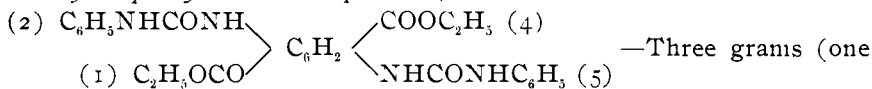
Ethyl diacetimino-succinylosuccinate was also prepared and some experiments conducted with it, but the acyl derivatives in this series are very much less stable, and we have not been able to obtain any heterocyclic condensations from them.

The work upon diaminophthalic acids, succinylosuccinic acid, and the naphthotetrazines is being continued.

Experimental.

The Preparation of p-Diaminoterephthalic Acid was carried out as described by Bogert and Dox¹, by converting ethyl succinylosuccinate into its diimine, oxidizing this to ethyl diaminoterephthalate, and saponifying the latter. In the oxidation of the diimine to the diamino ester by the action of bromine and sulphuric acid, the observation was made that the diimine must be added to the acid and not the acid to the diimine. If the latter order is followed, sufficient heat is generated to destroy much of the diimine, unless recourse is had to external cooling.

Ethyl Diphenyluraminoterephthalate,



molecule) of ethyl diaminoterephthalate were dissolved in 60 cc. of dry benzene in a flask provided with a return condenser and placed on the steam bath, and 2.83 grams (two molecules) of phenyl isocyanate added to the clear solution (excess of phenyl isocyanate appears to be without effect upon the result). After warming for a few minutes, the phenyluramino derivative began to separate as a light yellow precipitate, and in about fifteen minutes the reaction was complete, the yield being practically theoretical. The precipitate was filtered off, washed with dry benzene, recrystallized from nitrobenzene, washed well with hot alcohol, dried at 110° to constant weight, and analyzed with the following results:

Found: C, 63.22; H, 5.24; N 11.19. Calculated for $\text{C}_{26}\text{H}_{26}\text{O}_6\text{N}_4$: C, 63.93; H, 4.91; N, 11.47.

On account of the insolubility of this substance, it is difficult to thoroughly purify it, and this is the cause of the somewhat wide variation of the percentages found from those calculated.

¹ This Journal, 27, 1136 (1905).

The pure phenyluramino compound is a light yellow, crystalline solid, melting with decomposition at about 262°. It is very difficultly soluble in water, alcohol, carbon tetrachloride, ethyl acetate, amyl valerate, or benzene, but may be crystallized from nitrobenzene. Acetic anhydride gradually dissolves it with formation of acetyl derivatives of ethyl diaminoterephthalate.

When the phenyluramino ester was boiled with a freshly prepared alcoholic solution of sodium ethylate, a yellow sodium salt separated, which was dissolved in water and the solution precipitated by adding acetic acid. This precipitate may be the free phenyl uramino acid

$$\begin{array}{c} \text{C}_6\text{H}_5\text{NHCONH} \\ \text{HOOC} \end{array} \text{C}_6\text{H}_2 \begin{array}{c} \text{COOH} \\ \text{NHCONHC}_6\text{H}_5 \end{array}$$
, but not enough was obtained to identify it.

By heating the phenyluramino ester with a fifty per cent. aqueous solution of hydrazine hydrate in a sealed tube for four hours at 130°, a yellow amorphous substance was produced, not melting below 320°, insoluble, or very difficultly soluble in water or alcohol, and unchanged by six hours' boiling with acetic anhydride. It dissolved in dilute caustic alkali, and was re-precipitated from such solutions by acids. It has not been further studied.

When the phenyluramino ester is heated with aniline, a naphthotetrazine is formed, as described beyond.

Ethyl Tetracetyl-p-Diaminoterephthalate,

(1) ROOC $\begin{array}{c} \text{C}_6\text{H}_2 \\ \text{N}(\text{COCH}_3)_2 \end{array}$ (5) —The above phenyluramino
(2) (CH₃CO)₂N $\begin{array}{c} \text{C}_6\text{H}_2 \\ \text{COOR} \end{array}$ (4)

ester was boiled for about four hours with excess of acetic anhydride in a flask with a return condenser, when a clear, almost colorless, solution resulted. This solution was concentrated until crystals began to appear, when it was allowed to cool and the tetracetyl derivative crystallized out. During the concentration, the solution darkened somewhat. The crude product was purified by re-crystallization from alcohol, and gave the following results on analysis:

Found: C, 57.16 and 57.61; H, 5.83; N, 6.73. Calculated for C₂₀H₂₄O₈N₂: C, 57.14; H, 5.71; N, 6.66.

The by-products were acetanilide and carbon dioxide.

The pure substance forms colorless crystals melting at 207–208° (corr.), apparently insoluble in water, but soluble in alcohol or benzene.

Ethyl s-Diacetyl-p-Diaminoterephthalate,

(1) ROOC $\begin{array}{c} \text{C}_6\text{H}_2 \\ \text{NHCOCH}_3 \end{array}$ (5) —An excess of alcohol was
(2) CH₃CONH $\begin{array}{c} \text{C}_6\text{H}_2 \\ \text{COOR} \end{array}$ (4)

added to the mother liquor from the above tetracetyl derivative and the

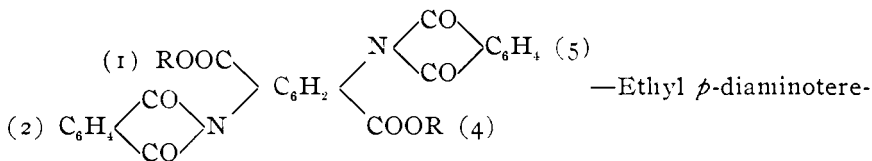
solution boiled. On cooling, the diacetyl derivative separated in large crystals. These were purified by re-crystallization from alcohol and treating with bone black, and the product analyzed:

Found: C, 57.07 and 57.48; H, 5.83 and 5.97; N, 8.50. Calculated for $C_{16}H_{20}O_6N_2$: C, 57.14; H, 5.95; N, 8.33.

The pure compound is yellowish white, with a decided greenish fluorescence, while the corresponding tetracetyl derivative is colorless and shows no trace of fluorescence. It melts at 219° (corr.), and is soluble in alcohol, benzene, and in most of the ordinary organic solvents.

When acetic anhydride was added to ethyl *p*-diaminoterephthalate itself, heat was evolved and the ester gradually went into solution. This solution was evaporated until crystals began to form (the color of the solution darkening somewhat during the concentration), and was then allowed to cool. The crystalline mass which separated was purified as before, and yielded the diacetyl derivative identical with that obtained from the phenyluramino ester. The formation of tetracetyl diaminoterephthalate was not, however, observed. The diacetyl derivative was also obtained when ethyl diaminoterephthalate was heated with acetyl chloride in presence of calcium carbonate. Boiling the diacetyl compound with phenylhydrazine or with benzylamine caused no change, but when it was heated with propylene diamine in a sealed tube for six hours at 150° , large yellow crystals separated on cooling. These crystals have not been further examined.

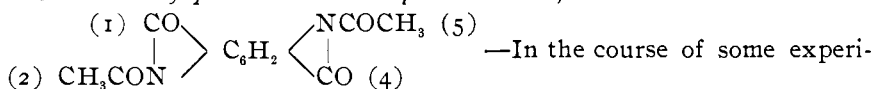
Ethyl p-Diphthalimidoterephthalate,



phthalate was fused with excess of phthalic anhydride, and the claret-colored melt when cold extracted repeatedly with boiling alcohol. There remained a cream colored crystalline residue, which softened slightly at 320° and melted at 326° (corr.). It is moderately soluble in hot benzene, difficultly soluble in toluene, and very difficultly soluble in chloroform.

Found: N, 5.70. Calculated for $C_{28}H_{20}O_8N_4$: N, 5.47.

When this compound was heated with aqueous ammonia in a sealed tube for four hours, at 150° , a dark-brown solution was formed. This was evaporated to dryness on the water-bath, and left a dark-brown hygroscopic mass. When the latter was carefully heated, a white crystalline sublimate collected, m. p. 228° (uncorr.), but not enough material was obtained for an analysis.

Di-lactam of p-Diacetaminoterephthalic Acid,

ments on the reduction of the benzene nucleus, an alcoholic solution of ethyl diacetyl-*p*-diaminoterephthalate was treated with sodium amalgam upon the water-bath. Instead of reduction, however, saponification occurred, and a sodium salt separated as a white precipitate. This was dissolved in water and the free acid precipitated by the addition of dilute acetic acid. The product was white, infusible, and insoluble in the ordinary organic solvents. Judging by its color and other properties, it may have been the diacetyl-*p*-diaminoterephthalic acid, for the free diaminoterephthalic acid is a yellowish green. This point will be cleared up later. On boiling the compound with acetic anhydride, it slowly dissolved, and on cooling white infusible flakes separated, which were purified with difficulty. The analysis gave the following figures:

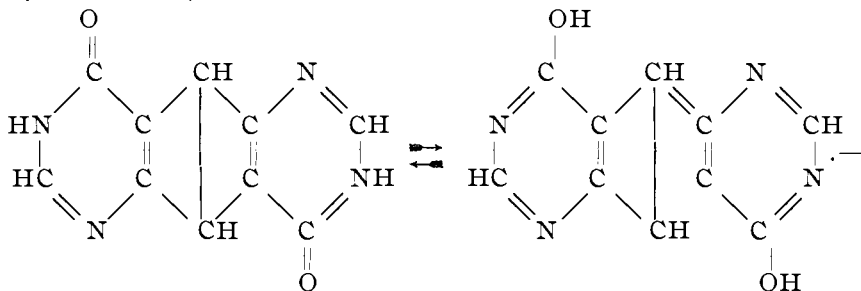
Found: N, 11.07. Calculated for $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_2$: N, 11.47.

Bogert and Dox¹ reported *p*-diaminoterephthalic acid as unchanged by boiling acetic anhydride. We have now found that when the diamino acid is boiled for some time with acetic anhydride, it gradually dissolves, and on cooling the same di-lactam crystallizes out as mentioned above, except that the crude product thus obtained is apt to be rather darker in color.

Found: N, 11.50. Calculated for $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_2$: N, 11.47.

For convenience, we shall designate this di-lactam as "di-acetantranil" in the experiments which follow.

4,9-Diketotetrahydro-1,3,6,8-naphthotetrazine (*4,9-Dihydroxy-1,3,6,8-naphthotetrazine*)²,



Seven grams of ethyl *p*-diaminoterephthalate and ten grams formamide were heated together in a sealed tube for seven hours at 200–210°. An

¹ This Journal, 27, 1127 (1905).

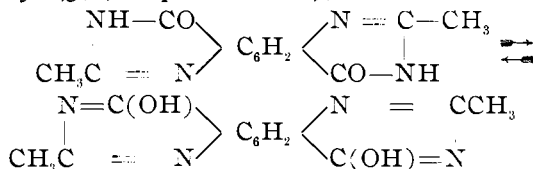
² This numbering of the nucleus is that adopted in Richter's "Lexicon," and the nomenclature in the previous articles by Bogert and Dox (loc. cit.) should be revised to correspond.—M. T. B.

excess of formamide was used in order that it might act also as solvent. At the close of the reaction, the tube was filled with a gray crystalline mass, which was purified by dissolving in dilute potassium hydroxide solution and reprecipitating with carbon dioxide. When thus purified, it appeared as an amorphous, pale yellow powder. The yield was theoretical.

Found: C, 55.91; H, 3.21; N, 26.20 and 25.94. Calculated for $C_{10}H_6O_2N_4$: C, 56.07; H, 2.80; N, 26.17.

The substance melts above 310° . It is insoluble, or very difficultly soluble, in water, alcohol, benzene, or the other usual neutral organic solvents. It evidently dissolves in formamide at high temperatures, for the crystals which separated in the tube were large and well formed, as well as being practically pure. It dissolves readily in dilute caustic alkalis, and is reprecipitated from such solutions by dilute acids or by carbon dioxide.

2,7-Dimethyl-4,9-diketotetrahydro-1,3,6,8-naphthotetrazine (2,7-Dimethyl-4,9-dihydroxy-1,3,6,8-naphthotetrazine),



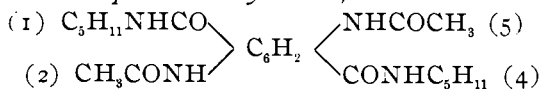
Ethyl diacetyl-*p*-diaminoterephthalate was heated with excess of alcoholic ammonia in a sealed tube for five or six hours at 200° . When cold, the tube contained a mass of greenish crystals. These were dissolved in dilute potassium hydroxide solution and reprecipitated by carbon dioxide. The precipitate was washed with hot water, dried at 110° , and analyzed:

Found: N, 22.47. Calculated for $C_{12}H_{10}O_2N_4$: N, 23.1.

Considerable difficulty was encountered in purifying this substance. When precipitated from alkaline solution by carbon dioxide, it separated as a mud, which was not easy to wash thoroughly, and the figure for nitrogen is therefore too low.

The dry substance is a pale yellow, amorphous powder, with a greenish cast, which melts above 325° .

*Diacetyl-*p*-diaminoterephthalisoamylamide,*

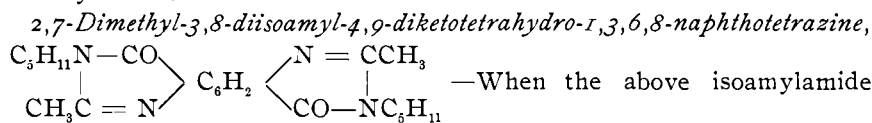


Ethyl diacetyl-*p*-diaminoterephthalate was heated with isoamylamine. A clear solution resulted, which deposited a white substance on cooling. This was recrystallized from dilute alcohol, and analyzed:

Found: N, 13.64. Calculated for $C_{22}H_{34}O_4N_4$: N, 13.4.

The pure compound forms long, colorless, silky needles, which soften at 246° (corr.) and melt at approximately 255° (corr.), apparently with partial conversion to the naphthotetrazine. The substance is insoluble in water, but dissolves in alcohol, benzene, and other organic solvents. Caustic alkalis change it to the corresponding naphthotetrazine.

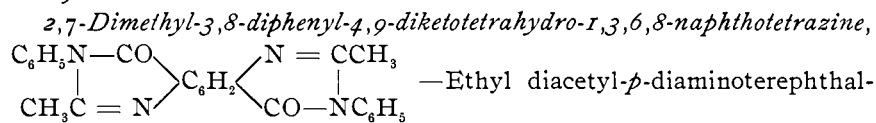
This same amide was obtained also from the diacetanthranil and isoamylamine.



was boiled for ten or fifteen minutes with a dilute potassium hydroxide solution, it changed considerably in appearance. On filtering out the product and recrystallizing it from alcohol, yellowish white needles, with greenish fluorescence, were obtained, melting at 179° (corr.).

Found: N, 14.64. Calculated for $\text{C}_{22}\text{H}_{30}\text{O}_2\text{N}_4$: N, 14.66.

Brominated in acetic anhydride solution, this tetrazine gave a yellowish white, crystalline bromine derivative, melting in the neighborhood of 290°.

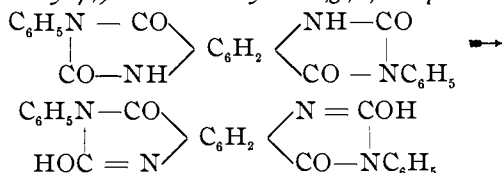


But when the diacetanthranil was heated for fifteen minutes with aniline, small yellow crystals separated from the solution on cooling. These were recrystallized from acetic anhydride, washed with alcohol, and dried; or, the crude product was easily purified by washing with boiling acetic acid and then with boiling alcohol.

Found: N, 14.29. Calculated for $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_4$: N, 14.21.

This is evidently the diphenylnaphthotetrazine sought, as the percentage of nitrogen in the corresponding amide is only 13.02. The pure substance crystallizes in pale greenish yellow leaflets, which do not melt at 325°. The compound is insoluble in alcohol or acetic acid, and very difficultly soluble in hot nitrobenzene.

3,8-Diphenyl-2,4,7,9-tetraketoctahydro-1,3,6,8-naphthotetrazine (*3,8-Diphenyl-2,7-dihydroxy-4,9-diketotetrahydro-1,3,6,8-naphthotetrazine*),



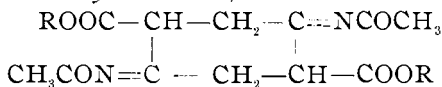
Ethyl diphenyluraminoterephthalate was heated with aniline in a sealed tube at 225° for six hours. Considerable decomposition was evident in the tube. By boiling the product with glacial acetic acid, the tarry impurities were removed, leaving a bright yellow crystalline residue.

Found: N, 13.99. Calculated for $C_{12}H_{14}O_4N_4$: N, 14.07.

The phenyluramino ester and aniline were also boiled together in an open test tube, but no reaction occurred.

The purified substance is yellow and crystalline, and does not melt below 330°. It is apparently insoluble in water, alcohol, or glacial acetic acid. In dilute caustic alkalis it dissolves, and is reprecipitated from such solutions by acetic acid.

Ethyl Diacetiminosuccinylosuccinate,



This substance is much less stable than the corresponding diacetyldiaminoterephthalate, and its preparation is hence more difficult. It was obtained as follows: A very slight excess of acetic anhydride was added to ethyl diiminosuccinylosuccinate, and caused but little rise of temperature. The mixture was carefully warmed until a clear solution resulted, which was then allowed to cool. The excess of acetic anhydride was neutralized with ammonia, and any excess of ammonia carefully neutralized with acetic acid. The crystalline product was purified by recrystallization from dilute alcohol, washing the crystals occasionally with a little ether. The loss in purification was considerable, and the final yield poor. The purified substance forms fluffy, white crystals, with a greenish fluorescence, which melt sharply at 215–216° (corr.), and are easily soluble in alcohol or benzene, but difficultly in ether. The same product was obtained by the action of acetyl chloride upon the diiminosuccinylosuccinate in presence of pyridine.

Found: N, 8.35. Calculated for $C_{16}H_{20}O_6N_2$: N, 8.3.

This compound was dissolved in alcohol, and boiled with sodium ethylate, thereby causing the gradual separation of a white sodium salt. This salt was dissolved in water, and acetic acid added. There resulted a white precipitate, apparently the free acid. It was very unstable and readily decomposed with evolution of carbon dioxide. This instability of the free acid is quite in line with that of the free succinylosuccinic acid itself. Not enough of the material was prepared for an analysis.

Ethyl Dibenzoyliminosuccinylosuccinate.—Ten grams of the diimino ester were dissolved in 75 gms. of pyridine, and 11 c. c. of benzoyl chloride added. When the reaction was completed, alcohol was added. A light-yellow precipitate separated, which was recrystallized from benzene, giving yellow, feathery needles. m. p. 255° (uncorr.).

Found: N, 6.6. Calculated for $C_{26}H_{26}O_6N_2$: N, 6.1. Difficulty was experienced in completely freeing the compound from traces of pyridine, and this is believed to be the cause of the rather high nitrogen percentage.

When dissolved in acetic anhydride, treated with bromine, and the temperature raised, a finely pulverulent, heavy precipitate separated on cooling, melting at 264° (uncorr.), which was probably the corresponding ethyl dibenzoylamino-terephthalate.

ORGANIC LABORATORY, COLUMBIA UNIVERSITY,
January, 1907.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY].
**THE RATE OF COMBUSTION AND PRESSURE DEVELOPED IN A
CALORIMETRIC BOMB¹**

BY FRANCIS G. BENEDICT AND FRANK. P. FLETCHER.

Received February 9, 1907.

The development of the high explosive industry has resulted in an unusually large number of tests of the force of the various explosives. For the most part, these tests, being designed to measure excessively high pressures, depend upon the expansion or compression of cylinders, capsules or rods of a metal or alloy. In the internal combustion engine the measurement of the force of the explosion is now accurately made with the ordinary indicator. So far as we are aware, no observations have been recorded regarding the pressures developed inside of a calorimetric bomb during the process of combustion. The early observations of Frankland² that complete combustion of carbon monoxide could be obtained by burning it in an atmosphere of oxygen, under pressure, has led to the rapid development of numerous forms of calorimetric bombs for the determination of the heat of combustion of various organic materials. The most noted of these bombs is that of Berthelot³ which has been modified in many ways by Hempel⁴, Atwater⁵, and Williams⁶.

The use of the calorimetric bomb has extended with great rapidity in the last few years, and observations regarding the development of pressure during combustion are of decided value in estimating the size of the bomb, thickness of the walls, and strength of other parts in their manufacture. The present proportions of the bomb are empirical, and undoubtedly with a very large safety factor. The large mass of metal now

¹ The expense of this research was in part borne by the Carnegie Institution of Washington.

² Pr. Roy. Soc. 16, 419 (1868).

³ *Traité pratique de calorimétrie chimique*, Paris (1893), p. 128.

⁴ *Gasanalytische Methoden* (1890), p. 355.

⁵ Bull. 21, Office of Experiment Stations, U. S. Dept. of Agriculture, (1895), p. 124. See also Atwater and Snell. *This Journal*, 25, 623. (1903).

⁶ See description in Wiley: *Principles and Practice of Agricultural Analysis*. Chem. Pub. Co. (1897), p. 570.