in shining, yellowish brown, silky needles. It is almost completely insoluble in water, but easily dissolves in alcohol. It melts at 200° to a greenish black liquid.

0.1889 gram gave 32.1 cc. N at 22° and 741 mm. Calculated for above formula, 18.75 per cent. N. Found, 18.67 per cent. N.

Isocalycanthine Nitrosamine, $C_{11}H_{13}N_2.NO$.—Like calycanthine, isocalycanthine contains an NH group, as it forms an insoluble nitrosamine when its hydrochloride is treated with sodium nitrite, but while calycanthine nitrosamine could be obtained in crystalline condition, the isocalycanthine compound could not be made to crystallize. It was purified by dissolving in pyridine and throwing the solution into much cold water.

It forms a yellowish amorphous powder, darkens at 99° and melts at 106–7°.

0.1597 gram gave 29.6 cc. N at 20° and 754 mm. Calculated for above formula, 20.72 per cent. N. Found, 20.93 per cent. N.

As a secondary base isocalycanthine ought to form a benzoyl and an acetyl compound. All methods so far tried failed to produce such compounds. Either the alkaloid did not react at all, or when higher temperatures were used, it completely resinified.

When digested with acetyl chloride in the cold for a few weeks a hydrochloride of a fine steel-blue color is produced. When heated with acetyl chloride in a sealed tube for 6 hours, a hydrochloride of a dark brown color is formed. With methyl iodide the alkaloid forms the hydriodide of the unchanged base together with two other compounds neither of which seems to have the composition of either the hydriodide of the tertiary base or the iodide of the quaternary base derived from isocalycanthine. I shall try to determine the nature of all these substances and report on them in my next paper. Digested with concentrated sulphuric acid isocalycanthine seems to form a sulphonic acid which is under investigation. The work is continued.

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STUDIES IN NITRATION, VI. NITRANILINE DERIVATIVES OF ORGANIC ACIDS.[1]

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Bishop Tingle and F. C. Blanck have described a large number of substances which they obtained by the action of nitrating agents on a

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[1] Previous papers have appeared as follows: Bishop Tingle and Blanck, *Am. Chem. J.*, **36**, 605 (1906); Bishop Tingle and Rolker, THIS JOURNAL, **30**, 822; Bishop Tingle and Blanck, *Ibid.*, **30**, 1395, 1587 (1908); Bishop Tingle and Rolker, *Ibid.*, **30**, 1764 (1908).

considerable variety of *N*-acyl anilines. Many of these substances were duly identified, but a considerable proportion of them required further study in order to determine their nature.

Preliminary experiments showed[1] that not infrequently, numerous difficulties were encountered in attempting to hydrolyze the compounds prepared by Bishop Tingle and Blanck. It was also found that reduction of the substances in question did not appear to be well adapted for the determination of their constitution. In these circumstances we decided to attack the problem from the synthetic side and also to investigate more closely certain of the compounds isolated by Bishop Tingle and Blanck.

Our synthetical work may be divided into two sections: To the one belong those experiments in which the isomeric nitranilines were mixed with various organic acids, in presence of a solvent, usually ethyl alcohol (50 per cent.). The solutions were allowed to evaporate at the ordinary temperature. After the disappearance of each third of the solvent any crystals which had deposited were removed and examined.

In the second series of experiments the acid and nitraniline were intimately mixed and the mixture fused, the heating being continued until all evidence of reaction had ceased.

The following acids were employed: formic, acetic, stearic, oxalic, succinic, tartaric, citric, benzoic, salicylic, phthalic and picric; in addition we investigated the nitration products of propanilide. In solution, *picric acid* was the only acid which showed evidence of the production of a compound with the nitranilines.

It was unnecessary for our purpose to carry out any experiments at higher temperatures with *formic* or *acetic acids* and the nitranilines, because all the nitranilides of these acids are well known.

The substances isolated by Bishop Tingle and Blanck[2] by the action on propanilide of nitric acid alone and also of a mixture of nitric and acetic acids, prove to be essentially unchanged propanilide. The material which they obtained from propanilide and a mixture of nitric and sulphuric acids is *propionic p-nitranilide*, $CH_3CH_2CONHC_6H_4NO_2$. It crystallizes in yellowish brown flakes, melting at 182°.

Stearic acid failed to react with any of the nitranilines, either in solution or when fused. By the action of nitric acid on stearanilide Bishop Tingle and Blanck[3] obtained a yellow substance which they did not investigate. A similar material was produced by the interaction of nitric acid, trichloracetic acid and stearanilide. We have examined these compounds

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[1] Bishop Tingle and Blanck, THIS JOURNAL, **30**, 1595 (1908).

[2] THIS JOURNAL, **30**, 1408.

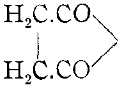
[3] *Loc. cit.*, p. 1409 (Exps. 65 and 66).

more closely and we find that they consist of impure stearanilide. No evidence of the formation of a nitro derivative could be obtained.

Oxalic acid failed to react with the nitranilines under the varied conditions which we employed.

The substances obtained by Bishop Tingle and Blanck,[1] by the action on oxanilide of nitric acid alone and also when mixed with trichloracetic acid, prove to be impure oxanilide.

The yellow material, produced under similar conditions by the action of a mixture of nitric and oxalic acids on oxanilide, is apparently the symmetrical oxo-*p*-nitranilide. It melts at 265°. The melting point mentioned in the literature is 260°.

We were unable to prepare compounds of *succinic acid* and *o*- or *p*-nitraniline, but by adding the acid to molten *m*-nitraniline *succino-m-nitrophenylimide*,  $\begin{array}{l} H_2C.CO \\ \;\;| \\ H_2C.CO \end{array} > NC_6H_4NO_2$, is produced. It was isolated in the form of pale yellow crystals, melting at 172°. The material obtained by Bishop Tingle and Blanck[2] from succinanil with mixtures of nitric and acetic and nitric and trichloracetic acids, respectively, proves to be unchanged anil. It was found, however, that the substance which they had prepared by the action of a mixture of nitric and oxalic acids on succinanilide was a dinitro derivative, melting at 240°–243°.

We were unable to synthesize any derivative of tartaric acid and *o*-nitraniline, but *m*-nitraniline gave *m-nitraniline tartaro-m-nitrophenylamidate*, $O_2NC_6H_4NHCOCH(OH)CH(OH)CO_2NH_3C_6H_4NO_2$. It is deposited in small, yellow crystals, melting at 172°. Under similar conditions of fusion, *p*-nitraniline yielded *tartaro-p-nitrophenylamidic acid*, $O_2NC_6H_4NHCOCH(OH)CH(OH)CO_2H$. It was obtained in bright yellow crystals, melting at 218°.

The compound obtained by Bishop Tingle and Blanck[3] from tartranilide and a mixture of nitric and oxalic acids proves to be *sym. tartaro-m-dinitranilide*, $O_2NC_6H_4NHCOCH(OH)CH(OH)CONHC_6H_4NO_2$. It melts at 224° and gives *m*-nitraniline when hydrolyzed by means of an aqueous solution of sodium carbonate.

The only derivative which we could prepare from citric acid and the nitranilines was one from the *m*-isomer. It is, apparently, a *di-m-nitraniline salt*, and is formed by fusion of the constituents. It is deposited in bright yellow crystals, melting at 207°.

An examination of the compound prepared by Bishop Tingle and Blanck by the action of a mixture of nitric and oxalic acids on citranilide

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[1] THIS JOURNAL, 30, 1588.

[2] *Loc. cit.*, p. 1589.

[3] *Ibid.*, p. 1591.

shows it to be *citratris-m-nitranilide*, $C_3H_5O(CONHC_6H_4NO_2)_3$. It melts at 122°. Their products obtained in a similar manner from mixtures of nitric and acetic acids and from nitric and trichloracetic acids, respectively, have been identified as impure citranilide.

Salicylic and *phthalic acids* failed to react with any of the nitranilines, either in solution or when fused. The same is true of *benzoic acid*, except that small quantities of a compound or compounds were formed when the acid was fused with *o*- and *m*-nitraniline, respectively. The material melted at a relatively high temperature and did not consist of either of the benzonitranilides. We did not pursue its investigation.

In solution *picric acid* and *o*-nitraniline fail to react, but the *m*- and *p*-isomers form *salts*, $O_2NC_6H_4NH_3OC_6H_2(NO_2)_3$; the former melts at 147°, the latter at 100°. Exactly the same results were obtained by fusion of picric acid with the respective nitranilines.

By the action of a mixture of nitric and oxalic acids on picranilide, Bishop Tingle and Blanck[1] prepared a compound which we have examined further. After purification it forms a bright yellow, granular powder, melting at 197°–200°. Analysis shows it to be a *picronitranilide* (*tetranitrodiphenylamine*) $O_2NC_6H_4NHC_6H_2(NO_2)_3$.

Bishop Tingle and Blanck's compound[1] from picranilide and nitric and trichloracetic acids is also a tetranitrodiphenylamine. After recrystallization from glacial acetic acid it melted sharply at 200°; when recrystallized again it melted at 213°.

Another *tetranitrodiphenylamine* was prepared by the same chemists[2] by dissolving diphenylamine in concentrated nitric acid. The crude product melts at 190–194° After recrystallization from nitrobenzene the melting point is 200°. This product was boiled with glacial acetic acid, but only a small portion dissolved; the residue melted at 275° and proved to be the tetranitro derivative.

The following tetranitrodiphenylamines are described in the literature: NO_2 = 2, 4, 6, 2′, m. about 220°; 2, 4, 6, 3′, m. 205°; 2, 4, 6, 4′, m. 216°; 2, 4, 2′, 4′, m. 180°; one of unknown constitution m. 192°. It is impossible to determine from the melting points whether our compounds are identical with any of these substances.

Bishop Tingle and Blanck have called attention[3] to the unsatisfactory nature of the current view regarding the constitution of the para derivatives of benzene. The results described above confirm their objections. In the case of the reactions which we have studied the reactivity of the nitranilines increases in the order ortho, para and meta. It appears reasonable to assume that the approximation of the NO_2 and NH_2 groups

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[1] *Loc. cit.*, p. 1411.

[2] *Ibid.*, p. 1405.

[3] *Ibid.*, p. 1595.

follows the same order, in which case, according to current ideas, they must be nearer together in paranitraniline than in the meta derivative. On theoretical grounds Hinrichs[1] reached the conclusion that the ortho positions are more remote than the para positions. It is hoped to throw some additional light on the question by means of the results of an investigation which is now in progress in this laboratory.

Experimental.

The experiments described below were all carried out with the respective acids and nitranilines in equimolecular proportion, unless otherwise stated. The investigations at the ordinary temperature were made in ethyl alcoholic solution. In special cases we tried the effect of other solvents, such as well-dried acetone or ethyl acetate, and we varied the percentage of water in the alcohol, but the results, in every instance, were essentially identical with those observed when 95 per cent. alcohol was employed.

The mixed solutions of acid and nitraniline were allowed to evaporate spontaneously, at the ordinary temperature, until one or two crystals appeared, the volume of liquid was then measured with approximate accuracy and the evaporation allowed to continue until one-third of the saturated solution had dissipated, the deposited crystals being then removed. One-half of the mother liquor was now allowed to evaporate and a second crop of crystals was collected; finally the residual liquid was permitted to dry up completely.

Each of these three crops of crystals was examined optically, and its melting point was determined, alone and also when mixed with one of the original constituents. Whenever it was judged to be necessary these individual fractions were recrystallized until we had been able to satisfy ourselves regarding the composition of the material with which we were dealing.

Our experiments at higher temperatures were carried out by intimately mixing equimolecular proportions of the constituents, which were in a finely divided condition, and fusing them by means of a bath of conc. sulphuric acid, until chemical action ceased. The solid products were then recrystallized in the ordinary manner.

1. EXPERIMENTS WITH FORMIC ACID.—From solution of this acid, essentially pure *o*-, *m*- and *p*-nitraniline were deposited.

2. EXPERIMENTS WITH ACETIC ACID.—The results were practically identical with those from formic acid. We did not think it necessary to carry out any experiments with either of these acids at a higher temperature because, of course, all the formo- and acetonitranilides are known.

3. EXPERIMENTS WITH PROPIONIC ACID.—The products obtained by Bishop Tingle and Blanck[2] from propanilide by the action of nitric acid alone (Exp. 59), and also by that of a mixture of nitric and acetic acids (Exp. 58), prove to be essentially propanilide. The substance which they prepared by means of a mixture of nitric and sulphuric acid (Exp. 57) is *propionic p-nitranilide*, $CH_3CH_2CONHC_6H_4NO_2$. It crystallizes from acetic anhydride in yellowish brown flakes, melting at 182°. Found, C 55.68, H 5.00. Calculated, C 55.60, H 5.15. When boiled with an aqueous solution of sodium carbonate it yields *p*-nitraniline.

4. EXPERIMENTS WITH STEARIC ACID.—Alike in solution at the ordinary temperature and also when fused, stearic acid affords no evidence of combination with *o*-, *m*-, or *p*-nitraniline. The constituents were isolated and identified beyond any question.

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[1] "Proximate Constituents of the Chemical Elements," St. Louis (1904), page 83.

[2] THIS JOURNAL, **30**, 1408.

This result caused us to examine the products obtained by Bishop Tingle and Blanck[1] from stearanilide with nitric acid alone (Exp. 65) and also when mixed with trichloracetic acid (Exp. 66).

A careful purification of substances in question showed that they consisted of impure stearanilide and that nitration had not taken place under the conditions employed by them.

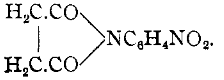
5. EXPERIMENTS WITH OXALIC ACID.—The products which we obtained from oxalic acid and the nitranilines, in alcoholic solution, and also those resulting from prolonged fusion of the acid with the nitranilines proved to be simply mixtures of the constituents.

We now took up the examination of substances obtained by Bishop Tingle and Blanck in the course of their experiments on the nitration of oxanilide.[2]

The yellow substance (m. p. 235–7°) which they observed in connection with the nitration in the presence of trichloracetic acid (Exp. 105) proved to be impure oxanilide.

The white powder (Exp. 106), obtained by the use of nitric acid alone, was also impure oxanilide.

The yellow compound, formed from oxanilide and nitric acid in presence of oxalic acid, after recrystallization from nitrobenzene melted at 265°. It was rather sparingly soluble in the ordinary media. Prolonged boiling with an aqueous solution of sodium carbonate hydrolyzed it to *p*-nitraniline showing that the compound is probably symmetrical oxo-*p*-nitranilide (oxobis-*p*-nitrophenylamide), the melting point of which is given in the literature as 260°.

6. EXPERIMENTS WITH SUCCINIC ACID.—No new compounds could be isolated by the action of succinic acid on any one of the nitranilines in solution. The acid does not appear to combine with either *o*- or *p*-nitraniline when the respective mixtures are fused. In the case of the *m*-isomer, however, it was found that combination takes place if the nitraniline is thoroughly melted and the acid added gradually, the heating being continued until evolution of steam ceases. The product consists of *succino-m-nitrophenylimide,*  $\begin{array}{l} H_2C.CO \\ \quad | \\ H_2C.CO \end{array}\!\!>NC_6H_4NO_2$. It is deposited in pale yellow crystals, melting at 172°. Found N, 12.87. Calculated, 12.72.

The substance (m. p. 156–8°) obtained by Bishop Tingle and Blanck[3] from succinanil, nitric acid and trichloracetic acid (Exp. 114), proved to be unchanged succinanil. The same is true of the product from nitric and acetic acids (Exp. 116). By repeated crystallization this preparation was obtained in deep red needles, melting sharply and constantly at 154°. It behaved in all ordinary respects like a pure compound, but the color was removed without difficulty by means of animal charcoal.

The substance obtained from succinanilide, oxalic acid and nitric acid[4] (Exp. 119) proved to be a *dinitro derivative.* After purification it melts at 240–3°. Found, C 53.91, H 4.24, N 15.25. Calculated for $C_{16}H_{14}O_6N_4$, C 53.67, H 4.00, N 15.6. Symmetrical succinobis-*p*-nitranilide melts at 260°.

7. EXPERIMENTS WITH TARTARIC ACID.—There is no evidence of the formation of any compound of tartaric acid and the nitranilines in solution and *o*-nitraniline does not appear to combine with the acid when the two are fused.

Fusion of the acid with *m*-nitraniline produces the salt, *m-nitraniline tartaro-m-nitrophenylamidate,* $O_2NC_6H_4NHCOCH(OH)CH(OH)CO_2NH_3C_6H_4NO_2$, which is deposited

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[1] *Loc. cit.*, 1409.

[2] THIS JOURNAL, **30**, 1588 (Exps. 105–7).

[3] *Loc. cit.*, p. 1589.

[4] *Ibid.*, 1590.

in small yellow crystals, melting at 172°. Found N, 13.91. Calculated, 13.72. It dissolves easily in an aqueous solution of sodium hydrogen carbonate and on acidification of the liquid *m*-nitraniline is deposited.

Under similar conditions *p*-nitraniline yielded *tartaro-p-nitrophenylamidic acid*, $O_2NC_6H_4NHCOCH(OH)CH(OH)CO_2H$, which was deposited in bright yellow crystals, melting at 218°. Found, N 10.49. Calculated, 10.37.

The compound obtained by Bishop Tingle and Blanck[1] by the action of a mixture of nitric and oxalic acids on tartranilide (Exp. 123), after purification, was deposited as a pale yellow, microcrystalline powder, melting at 224°. It appears to be the symmetrical *m-dinitranilide*, $O_2NC_6H_4NHCOCH(OH)CH(OH)CONHC_6H_4NO_2$. Found, C 48.93, H 3.70. Calculated, C 49.2, H 3.59. When boiled with an aqueous solution of sodium carbonate it yields *m*-nitraniline.

8. EXPERIMENTS WITH CITRIC ACID.—No compound could be obtained from citric acid and *o*- or *p*-nitraniline either in solution or by fusion. *m*-Nitraniline also failed to react in solution, but when heated with the acid at about 15–20° above its melting point, during 1.5 hours, a compound was obtained which separates from an alcoholic solution in bright yellow crystals, melting at 207°. As might be expected, the analytical results are not entirely satisfactory, but they indicate that the compound is a *bis-nitraniline salt*, $C_3H_5O(CO_2H)_3.2NH_2C_6H_4NO_2$. Found, C 46.90, H 3.48, N 11.22. Calculated, C 46.10, H 4.10, N 11.90.

An examination of the substances obtained by Bishop Tingle and Blanck[1] by the action on citranilide of mixtures of nitric and acetic acids (Exp. 127) and of nitric and trichloracetic acids (Exp. 129), respectively, showed that they were impure citranilide. The compound produced by the interaction of citranilide with citric and oxalic acids (Exp. 128) proves to be *citratris-m-nitranilide*, $C_3N_5O(CONHC_6H_4NO_2)_3$. It is deposited in yellowish granules melting at 122°. Found, C 51.92, H 3.60. Calculated, C 52.10, H 3.60. When boiled with an aqueous solution of sodium carbonate the compound is hydrolyzed to *m*-nitraniline.

9. EXPERIMENTS WITH BENZOIC ACID.—This acid failed to react with the nitranilines in solution. When fused with *o*- or *m*-nitraniline a substance or substances having a high melting point is produced in small quantity. No reaction takes place when the acid and *p*-nitraniline are fused together. We did not continue our experiments further in this direction because, of course, all the benzonitranilides are well known.

10. EXPERIMENTS WITH SALICYLIC ACID.—We were unable to obtain any evidence to show that salicylic acid combined with the nitranilines either in solution or when the acid and amine are fused together.

11. EXPERIMENTS WITH PHTHALIC ACID.—The above remarks regarding salicylic acid apply without modification to phthalic acid.

12. EXPERIMENTS WITH PICRIC ACID.—*o*-Nitraniline and picric acid do not appear to combine when solutions of the two are mixed, but *m*- and *p*-nitraniline yield salts under these conditions. *m-Nitraniline picrate*, $O_2NC_6H_4NH_3OC_6H_2(NO_2)_3$, is deposited from alcohol or ethyl acetate, as a reddish brown powder, melting at 147°. Found, N 19.078. Calculated, 19.073. When treated with an aqueous solution of sodium hydroxide and the alkaline liquid acidified, picric acid is precipitated.

p-Nitraniline picrate is deposited from alcohol in reddish yellow leaflets melting at 100°. Found, N 19.41. Calculated, 19.07.

We were unable to obtain any compound of *o*-nitraniline and picric acid by fusion of a mixture of the two substances. Fusion of picric acid with *m*- and *p*-nitraniline, respectively, leads to the production of the two additive compounds (salts) described above.

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[1] *Loc. cit.*, p. 1591.

The bright yellow compound obtained by Bishop Tingle and Blanck[1] by the action of a mixture of nitric and oxalic acids on picranilide (Exp. 96) after recrystallization from alcohol is deposited as a bright yellow, granular powder, melting at 197–200°. Found, C 41.29, H 2.01, N 19.88. Calculated, C 41.26, H 2.00, N 20.05. These results indicate that the compound is a picronitranilide (tetranitrodiphenylamine), $O_2NC_6H_4NHC_6H_2(NO_2)_3$.

By the action of a mixture of nitric and trichloracetic acids on picranilide, Bishop Tingle and Blanck[1] obtained a yellow substance (Exp. 95). After recrystallization from glacial acetic acid it melts sharply at 200°. When recrystallized again from the same solvent the melting point was 213°. Found, C 40.47, H 2.09. This substance is evidently a tetranitrodiphenylamine, but we are unable to state positively whether it is isomeric or identical with the preceding compound.

Another *tetranitrodiphenylamine* is prepared according to the method of Bishop Tingle and Blanck[2] by dissolving diphenylamine in concentrated nitric acid and pouring the solution into cold water. The crude product melts at 190–194°. After recrystallization from nitrobenzene it melts at 200°. When boiled with glacial acetic acid only a small portion dissolves, the residue melts at 275° and analysis shows it to be a *tetranitro derivative.* Found, C 41.40, H 1.84, N 19.57. Calculated, C 41.26, H 2.00, N 20.05, We made numerous attempts to hydrolyze the compound but they were unsuccessful. The substance is easily reduced by tin and hydrochloric acid; the product is extremely readily soluble and is quickly oxidized by air. Hitherto we have been unable to obtain any crystalline derivatives from this reduction product.

The investigation is being continued in this laboratory.

Summary.

1. We have investigated the interaction, under varied experimental conditions, of the three isomeric nitranilines with formic, acetic, stearic, oxalic, succinic, tartaric, citric, benzoic, salicylic, phthalic and picric acids.

2. The nitration products of the anilides of most of the above acids, and also the nitration products of propanilide and diphenylamine, which were prepared by Bishop Tingle and Blanck, have been examined in detail and their constitution has been determined.

3. A considerable number of new compounds have been prepared. The work will be continued in this laboratory during the coming academic year.

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THE ANHYDRIDES OF ISOPHTHALIC AND TEREPHTHALIC ACIDS.

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The anhydride of ortho-phthalic acid is obtained very easily by means of the usual methods for the preparation of anhydrides. It is also obtained by simply heating the acid. No anhydrides of the isomeric meta-

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[1] *Loc. cit.*, p. 1411.

[2] *Ibid.*, p. 1405.

[3] Read at the New Haven meeting of the Am. Chem. Soc., July, 1908.