

alcohol in minute, salmon crystals, melting with slight effervescence at 232.5° (cor.); insoluble in water, but soluble in dilute ethyl alcohol. Yield, 1 gram from 2 grams quinazolone.

Calculated for $C_{10}H_{17}ON_2I$: I, 30.51.

Found: I, 30.43.

2-m-Methoxy-p-hydroxystyryl-4-quinazolone and Methyl Iodide were heated together for 3 hours at 120°. The crude product crystallized from methyl alcohol in salmon red, microscopic crystals, melting quietly at 223–5° (uncor.); difficultly soluble in water, but soluble in dilute alcohol. Yield, 2.5 grams from 2 grams quinazolone.

Calculated for $C_{18}H_{17}O_2N_2I$: I, 29.11.

Found: I, 28.82.

ORGANIC LABORATORY, COLUMBIA UNIVERSITY.
NEW YORK CITY.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY
No. 206.]

p-AMINOBENZONITRILE AND CERTAIN OF ITS DERIVATIVES.

[THIRD PAPER.]¹

BY MARSTON TAYLOR BOGERT AND LOUIS ELSBERG WISE.

Received March 18, 1912.

In continuing the work on *p*-aminobenzonitrile previously reported² from this laboratory, the authors have prepared and studied the following new compounds: *p*-aminobenzonitrile picrate, *p*-nitrobenzoyl-*p*-aminobenzonitrile, *p*-cyanophenyl urethane, *p*-carbamidophenyl urethane, *p*-cyanophenyl urea, *p*-cyanocarbanilide, di-*p*-cyanocarbanilide, *p*-cyanoxanilamide, oxanilic *p*-cyananilide, *p*-cyanosuccinanic acid, its silver salt, methyl and ethyl esters, *p*-cyanosuccinil, *p*-cyanophthalanilic acid, *p*-cyanophthalanil, a formaldehyde condensation product, bromo-*p*-acetaminobenzonitrile, 3-nitro-4-acetaminobenzamide, 3,4-diacetyldiaminobenzonitrile, cyano- α -methylbenzimidazole and the corresponding carbamidomethylbenzimidazole.

Of these compounds, the picrate was obtained by bringing the nitrile and picric acid together in benzene solution; the *p*-nitrobenzoyl derivative, by the action of *p*-nitrobenzoyl chloride upon the nitrile in presence of pyridine. From the aminonitrile and ethyl chlorformate, the cyanophenyl urethane was obtained, whose CN was hydrolyzed to a $-\text{CO.NH}_2$ group by the action of an alkalin solution of hydrogen dioxide. *p*-Cyanophenyl urea could not be prepared from the urethane and ammonia, but was obtained from the hydrochloride of the nitrile and potassium cyanate. From the aminonitrile and phenyl isocyanate, the *p*-cyanocarbanilide resulted; and, with phosgene, the di-*p*-cyanocarbanilide.

¹ Read at the Washington Meeting of the Society, Dec. 29, 1911.

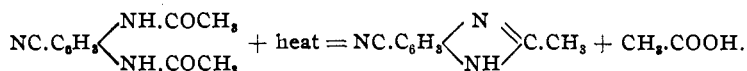
² THIS JOURNAL, 25, 478 (1903); 32, 1494 (1910).

Ethyl *p*-cyanooxanilate and ammonia yielded the corresponding amide, and aniline the anilide. By heating the aminonitrile with the anhydride of succinic or of phthalic acid, the anilic acids were produced, which, on treatment with acetic anhydride, gave the anils.

Formaldehyde condensed with the aminonitrile apparently to a diphen-amine of the structure $\text{CH}_2(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CN})_2$, without the formation of any monomolecular condensation of the type $(\text{CH}_2 : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CN})_x$.

Bromination of the acetaminonitrile, like nitration, yielded the mono-substituted product.

From the diacetyldiaminonitrile, the cyanomethylbenzimidazole was obtained by the action of heat, the condensation being accomplished by the elimination of a molecule of acetic acid:



Many of the acids corresponding to the above nitriles have been described by other investigators and will be found in the literature.

Experimental.

p-Aminobenzonitrile was prepared as described in our previous paper,¹ the nitrile being purified by crystallization from water. Instead of attempting to recover the nitrile in the mother liquors by concentration, it was found much more convenient to heat these aqueous mother liquors direct with excess of acetic anhydride, the nitrile being then thrown out in a few minutes as the crystallin acetyl derivative.

Picrate.—1.8 grams of picric acid were dissolved in benzene and a gram of the powdered nitrile added. The mixture was heated for a few minutes, filtered, and the filtrate concentrated. On cooling, the picrate separated in small yellow granular arborescent crystals which, after two re-crystallizations from dilute alcohol, appeared in long, silky, golden yellow needles, melting at 150.5° (cor.), with marked softening about four degrees lower. The substance is easily soluble in hot alcohol, in nitrobenzene or in acetone; moderately soluble in boiling water, in chloroform or in benzene; and very difficultly soluble in ether or in carbon tetrachloride.

Calculated for $\text{C}_{13}\text{H}_9\text{O}_7\text{N}_5$: N, 20.18. Found: N, 20.39.

The following additional information has been gained concerning the solubilities of certain compounds described in our previous papers and may be of service to future workers in this field:

p-Acetaminobenzonitrile is very easily soluble in cold acetone, boiling chloroform, boiling isoamyl alcohol, ethyl acetate, nitrobenzene or hot water; less readily soluble in cold alcohol, glacial acetic acid, or boiling

¹ THIS JOURNAL, 32, 1495 (1910).

isoamyl acetate; moderately soluble in boiling benzene; difficultly soluble in ether; and practically insoluble in carbon tetrachloride.

p-Acetaminobenzamide is readily soluble in boiling water, alcohol or nitrobenzene, crystallizing from the latter on cooling. It is very difficultly soluble in hot benzene, and practically insoluble in boiling ether, acetone or chloroform.

p-Benzoylaminobenzonitrile is easily soluble in cold acetone, hot ethyl or isoamyl alcohols; moderately soluble in cold chloroform, ethyl or isoamyl acetates, or in hot benzene; difficultly soluble in hot water or carbon tetrachloride; and very difficultly soluble in ether.

p-Nitrobenzoyl-*p*-aminobenzonitrile, $O_2N.C_6H_4.CO.NH.C_6H_4.CN$, was obtained from *p*-aminobenzonitrile and *p*-nitrobenzoyl chloride, in presence of pyridine, completing the reaction by a few minutes' boiling, then cooling, and pouring the mixture into a large volume of cold water. The precipitated nitrobenzoyl derivative was filtered out, washed with water and with sodium carbonate solution, and crystallized from 95% alcohol. Long, pale yellow, glistening needles resulted, melting at $258-9^\circ$ (uncor.); readily soluble in hot glacial acetic acid or in nitrobenzene; moderately soluble in cold acetone; rather difficultly soluble in boiling alcohol; very slightly soluble in hot water; and practically insoluble in ether, chloroform or benzene, at their boiling-points.

Calculated for $C_{14}H_9O_3N_3$: N, 15.74. Found: N, 15.83.

p-Cyanophenyl Urethane, $NC_6H_4.NHCOOC_2H_5$. The aminonitrile was dissolved in alcohol, the solution diluted, some sodium carbonate added, and then ethyl chlorformate. No action was evident in the cold, but on warming carbon dioxide was evolved and the urethane precipitated in colorless crystals. If sufficient water is not present, some of the product separates as an oil. Treatment of this oil with more water changes it to the crystallin urethane. The product was thoroughly washed with water, re-crystallized twice from dilute alcohol, dried to constant weight, and analyzed:

Calculated for $C_{10}H_{10}O_2N_2$: N, 14.74. Found: N, 15.00.

The pure compound forms colorless, glassy needles, melting at $116-7^\circ$ (cor.), with a faint pineapple odor, and soluble in cold acetone, benzene, methyl or ethyl alcohol, ether or chloroform. In boiling water it first melts to an oil, then slowly dissolves.

p-Carbamidophenyl Urethane, $H_2N.CO.C_6H_4.NHCOOC_2H_5$.—*p*-Cyano-phenyl urethane was heated for several hours at 100° with an aqueous solution of hydrogen dioxide (3%) made alkaline with sodium carbonate. The insoluble product was filtered out, washed with a small amount of alcohol, and crystallized thrice from dilute alcohol.

Calculated for $C_{10}H_{12}O_3N_2$: N, 13.46. Found: N, 13.64.

The pure substance crystallizes in slender, colorless, silky needles,

soluble in cold, glacial acetic acid, alcohol, hot benzene, or boiling water; difficultly soluble in boiling ether, acetone or chloroform. The melting point of the compound varies somewhat with the rate of heating. Heated quickly, it melts at about 232.5° (uncor.), but soon thereafter re-solidifies as the temperature rises, with evolution of ammonia. By treatment with chloroform, two substances were separated from this re-solidified melt, one of which remained unfused at 305° (uncor.), and was apparently insoluble in the ordinary solvents, but lack of material precluded further investigation along this line.

Digestion of the urethane with concentrated ammonia, or with a strong (33%) aqueous solution of methylamine, was without effect, no *p*-cyanophenyl urea being formed.

p-Cyanophenyl Urea, $\text{NC}_6\text{H}_4\text{NH.CO.NH}_2$.—The pulverized hydrochloride of *p*-aminobenzonitrile was dissolved in warm water and an aqueous solution of the calculated amount of potassium cyanate added. The urea precipitated immediately. It was filtered out, and purified by treating its aqueous solution with bone-black and re-crystallizing twice from water. The pure compound crystallizes in minute, colorless needles, melting at 207.5 – 208.5° (uncor.); easily soluble in hot ethyl or isoamyl alcohol; soluble in boiling acetone or in hot water; and apparently insoluble in ether, chloroform or benzene.

Calculated for $\text{C}_8\text{H}_7\text{ON}_3$: N, 26.09. Found: N, 26.24.

p-Cyanocarbanilide, $\text{NC}_6\text{H}_4\text{NH.CO.NHC}_6\text{H}_5$.—*p*-Aminobenzonitrile was dissolved in dry benzene and excess of phenyl isocyanate added. As no action appeared in the cold, the temperature was gradually raised to 100° . A yellow, crystallin solid soon separated. The mixture was allowed to stand over night, the precipitate removed, and crystallized from dilute alcohol until the melting point remained constant at 198.5° (cor.). The compound crystallizes in light, feathery clusters of colorless, silky needles, readily soluble in cold acetone, glacial acetic acid or alcohol; soluble in hot benzene or in cold chloroform; slightly soluble in ether; and very difficultly soluble in water. The yield is good.

Calculated for $\text{C}_{14}\text{H}_{11}\text{ON}_3$: C, 70.85; H, 4.68; N, 17.73.

Found: C, 70.32; H, 4.98; N, 17.37.

These poor results are due in part to the fact that the dry substance was so very light and fluffy that considerable difficulty was experienced in transferring it without loss from the balance to the combustion tube.

Di-p-cyanocarbanilide, $(\text{NC}_6\text{H}_4\text{NH})_2\text{CO}$.—The aminonitrile was dissolved in dry benzene and a benzene-toluene solution of phosgene added. A yellow precipitate separated almost immediately. The mixture was left over night, and the precipitate then filtered out and crystallized from dilute alcohol, from which it separated in small, colorless needles, melting at 273° (uncor.), with slight previous softening, soluble in hot alcohol;

difficultly soluble or insoluble in water, chloroform or ether. Yield, only fair.

Calculated for $C_{15}H_{10}ON_4$: N, 21.38. Found: N, 21.28.

p-Cyanooxanilamide, $NC_6H_4.NH.CO.CO.NH_2$.—Ethyl *p*-cyanooxanilate was warmed for a half hour with excess of concentrated ammonium hydroxide solution, then diluted with water and allowed to stand over night. The colorless, crystallin solid was filtered out, and crystallized from glacial acetic acid, giving minute, colorless crystals, melting above 300° , soluble in hot nitrobenzene; very slightly soluble in boiling alcohol; and practically insoluble in water, ether, chloroform, isoamyl acetate or benzene.

Calculated for $C_{16}H_{12}O_2N_3$: N, 22.23. Found: N, 22.32.

Oxanilic-p-Cyanooxanilide, $NC_6H_4.NH.CO.CO.NHC_6H_5$.—Ethyl *p*-cyanooxanilate was boiled for about 15 minutes with aniline and zinc chloride. When cold, the solidified melt was extracted with boiling alcohol. From the alcoholic extracts, crystals were obtained which were purified by dissolving them in boiling glacial acetic acid, filtering, and carefully diluting the filtrate with water. On cooling, crystals separated which were then crystallized from alcohol. As thus purified, the compound forms minute, colorless crystals, melting at 246° (uncor.); soluble in cold chloroform, but practically insoluble in water or ether.

Calculated for $C_{15}H_{11}O_2N_3$: N, 15.85. Found: N, 15.93.

p-Cyanosuccinanic Acid, $NC_6H_4.NH.CO.CH_2.CH_2.COOH$.—Four grams *p*-aminobenzonitrile and 3.5 grams freshly distilled succinic anhydride were brought together in chloroform solution and the whole boiled for half an hour. A crystallin precipitate gradually separated. The mixture was allowed to cool, the precipitate removed, and the filtrate boiled again. Another crop of crystals was obtained, which was removed and the filtrate again heated. This was continued so long as any additional product was obtained. The various crops of crystals, combined and washed with ether or chloroform, amounted to 4.6 grams and were practically pure. Recrystallized from water, the compound forms colorless minute prisms, melting at $213-214^\circ$ (uncor.); soluble in acetone, hot alcohol, boiling water or glacial acetic acid; insoluble in ether, chloroform or benzene.

Calculated for $C_{11}H_{10}O_2N_2$: N, 12.85. Found: N, 12.94.

It is easily soluble in aqueous solutions of ammonia or of the alkali carbonates, and gives a deep, reddish brown solution with ferric chloride, which, after heating for a short time and cooling, precipitates a brown iron salt.

Silver Salt.—The acid was dissolved in a slight excess of ammonium hydroxide solution, the solution warmed, silver nitrate added in excess, and the solution boiled to expel excess of ammonia. On cooling, the

silver salt separated in faintly colored needles, and another crop, of colorless and purer crystals, was obtained from the mother liquor. The salt is easily soluble in ammonium hydroxide solutions, slightly soluble in hot water but practically insoluble in cold.

Calculated for $C_{11}H_9O_3N_2Ag$: Ag, 33.20. Found: Ag, 33.36.

Methyl Ester.—The acid was esterified by suspending it in absolute methyl alcohol and passing in dry hydrogen chloride gas until complete solution resulted, and then pouring this solution upon cracked ice. The colorless, crystallin precipitate which separated was removed, washed thoroughly with sodium carbonate solution, then with water, and recrystallized from dilute methyl alcohol, giving delicate, lustrous, pearly leaflets, melting at $155-156^\circ$ (cor.) with very slight previous softening; easily soluble in cold chloroform or acetone; soluble in hot methyl alcohol, in boiling water or ether; apparently insoluble in the lower petroleum fractions.

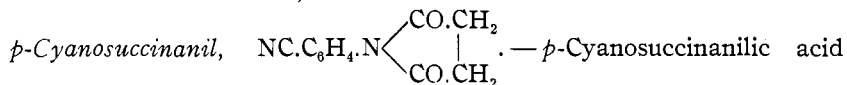
Calculated for $C_{12}H_{12}O_3N_2$: N, 12.07. Found: N, 12.24.

The *Ethyl Ester*, prepared in a similar manner, crystallizes from very dilute alcohol in colorless shining scales, melting at 111° (cor.); readily soluble in chloroform or acetone; soluble in alcohol, ether or hot benzene; insoluble in petroleum ether.

Calculated for $C_{13}H_{14}O_3N_2$: N, 11.38. Found: N, 11.54.

In preparing this ester, if too large an amount of alcohol is used in the esterification, the product is not precipitated when the solution is poured upon cracked ice.

In the course of these esterifications, the formation of imino esters, or of esters of bibasic acids, was not observed.



was added to excess of hot acetic anhydride, and the resulting solution evaporated to small volume. Some water was added, the mixture heated, filtered hot, and from the filtrate on cooling the anil separated in large crystals. Recrystallized repeatedly from water, opaque, ivory colored, coarse crystals were obtained, melting at 170° (cor.); soluble in cold acetone or chloroform, boiling alcohol, hot water, benzene, glacial acetic acid, isoamyl acetate or isoamyl alcohol; apparently insoluble in ether.

Calculated for $C_{11}H_9O_3N_2$: N, 14.00. Found: N, 14.05.

p-Cyanophthalanilic Acid, $NC_6H_4.NH.CO.C_6H_4.COOH(o)$.—3.1 grams phthalic anhydride were dissolved in 50 cc. chloroform, a solution of 2.5 grams *p*-aminobenzonitrile in 25 cc. chloroform added, and the mixture heated to boiling. Nearly colorless, silky needles separated from the boiling solution. On filtering out these needles and boiling the mother liquor, another crop of crystals was obtained; and this was

continued until nothing further separated from the mother liquor on boiling. Total yield, 5 grams. The various crops of crystals were combined and recrystallized from chloroform, giving fine colorless needles, very easily soluble in alcohol or ether; soluble in glacial acetic acid, warm acetone, hot isoamyl acetate, boiling water, boiling benzene or toluene; and appreciably soluble in cold chloroform. When heated sufficiently high, the substance loses water and forms the anil. The melting point, therefore, varies with the rate of heating. If plunged in a bath at 145°, it melts at about 163°, and soon thereafter the anil begins to sublime in the upper part of the tube.

Calculated for $C_{15}H_{10}O_3N_2$: N, 10.53. Found: N, 10.73.

p-Cyanophthalanil, $NC_6H_4.N \begin{array}{c} \diagup CO \diagdown \\ \diagdown CO \diagup \end{array} C_6H_4$, was formed, as just stated,

when *p*-cyanophthanic acid was heated above its melting point. The following, however, was found to be a better method of preparation: The anilic acid was added gradually to an excess of acetic anhydride, the solution evaporated to crystals, excess of anhydride destroyed by warming the crystallin mass with water, and the crude product recrystallized from alcohol. Feathery clusters of colorless silky hairs resulted, melting at 187° (cor.); readily soluble in glacial acetic acid, benzene, toluene, nitrobenzene, chloroform, acetone, boiling ethyl or isoamyl alcohol; soluble in ether or isoamyl acetate; and difficultly soluble in hot water. It sublimes readily and seems to be volatil with steam.

Calculated for $C_{15}H_8O_2N_2$: N, 11.29. Found: N, 11.44.

Formaldehyde Condensation Product.—One gram *p*-aminobenzonitrile was dissolved in acetone and about 3 cc. of aqueous formaldehyde solution were added. As nothing precipitated on standing, the solution was concentrated and water added. A syrupy sticky mass settled out, over which was a layer of fine colorless needles. When the sticky mass was boiled with water, practically all of it dissolved and, on cooling, more of the colorless needles were obtained. These needles were recrystallized several times from water, then dissolved in acetone, reprecipitated with water, and dried in a vacuum. They then melted at about 158° (uncor.), and under the microscope appeared as fine colorless hairs. The substance is easily soluble in acetone, hot alcohol or boiling chloroform; soluble in hot, but very difficultly soluble in cold water.

Calculated for $C_{15}H_{12}N_4$: N, 22.58. Found: N, 22.21, 22.60.

This would correspond to a methylene di(*p*-cyanophenamine) of the structure $CH_2(NH.C_6H_4.CN)_2$.

Under similar conditions, using anthranilic nitrile, Grube¹ obtained a derivative of the type $(CH_2 : N.C_6H_4.CN)_x$.

¹ *Inaug. Dissert., Marburg, 1909.*

Bromo-p-acetaminobenzonitrile, $(4) \text{CH}_3\text{CONH}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CN}(1)$.—*p*-Acetaminobenzonitrile was dissolved in warm, moderately strong acetic acid, excess of bromine added gradually, the mixture let stand over night, and excess of bromine then removed by boiling. The solution was largely diluted with water and the precipitated bromo compound crystallized repeatedly from 95% alcohol. The compound crystallizes in colorless glassy needles, occasionally united in rosetts, melting at $161.5\text{--}162.5^\circ$ (cor.), easily soluble in hot alcohol, in chloroform, acetone or glacial acetic acid; slightly soluble in boiling ether or carbon tetrachloride; difficultly soluble in water. The location of the bromine was not determined.

Calculated for $\text{C}_8\text{H}_7\text{ON}_2\text{Br}$: N, 11.72; Br, 33.44. Found: N, 11.80; Br, 33.99.

3-Nitro-4-acetaminobenzamide, $\text{CH}_3\text{CONH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CONH}_2$.—3-Nitro-4-acetaminobenzonitrile was heated for an hour or two with an alkaline hydrogen dioxide solution (3%). A small amount of acetic anhydride was added, to reacylate any nitroaminonitrile formed, and the whole evaporated to dryness. The residue was washed thoroughly with water and crystallized from alcohol, giving lustrous yellow scales. On further recrystallization from alcohol, flat, yellow, branching needles were obtained instead of scales. These needles softened and sublimed at about 215° , finally melting at 239.5° (uncor.) in a sealed capillary tube.

Calculated for $\text{C}_8\text{H}_6\text{O}_4\text{N}_3$: N, 18.84. Found: N, 18.84.

The compound is soluble in hot, less so in cold alcohol; very slightly soluble in boiling chloroform; appreciably soluble in boiling water; and apparently insoluble in cold water, cold chloroform, boiling benzene or boiling ether. Heated with aqueous potassium hydroxide, it yields the nitroaminobenzoic acid.

Thieme¹ endeavored to prepare this amide by the action of aqueous or of alcoholic ammonia upon the nitroacetaminobenzoic ester, but was unsuccessful, the acetyl group being split off each time.

3,4-Diacetaminobenzonitrile, $(\text{CH}_3\text{CONH})_2\text{C}_6\text{H}_3\cdot\text{CN}$.—The diamionitrile was treated with acetic anhydride and the solution warmed. A colorless precipitate soon separated. Water was then added and the mixture boiled, to destroy excess of acetic anhydride and to dissolve the crude acetyl derivative. The solution was filtered hot and from the filtrate on cooling, the acetyl derivative crystallized. It was purified by repeated recrystallization from water, decolorizing with bone-black, and then appeared as colorless, silky hairs, soluble in glacial acetic acid, alcohol or boiling water; difficultly soluble in hot chloroform or in benzene; practically insoluble in ether.

Calculated for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3$: N, 19.35. Found: N, 19.17.

The pure substance melts at $238\text{--}238.5^\circ$ (uncor.), and in the neighbor-

¹ *J. prakt. Chem.*, [2] 43, 457 (1891).

hood of 240° loses acetic acid with formation of the cyanbenzimidazole. If heated to 250-60°, charring results.

Cyano-α-methylbenzimidazole, $\text{NC.C}_6\text{H}_3 \begin{array}{l} \diagup \text{NH} \\ \diagdown \text{N} \end{array} \text{C.CH}_3$.—The preparation

of this imidazole was attempted by the following methods:

1. By reduction of 3-nitro-4-acetaminobenzonitrile. Reduction with stannous chloride and hydrochloric acid gave only the diaminobenzonitrile.

2. By the action of acetic acid on the diaminobenzonitrile.—0.53 gram of the crude diaminonitrile was boiled for an hour and three-quarters with a large excess of glacial acetic acid. The excess of acid was then partly removed by distillation and the residual solution made alkaline with sodium carbonate. A nearly colorless product separated. This was collected with ether, in which it dissolves with difficulty, and the ether then driven off. The residue was purified by repeated crystallization from water, and formed a colorless granular solid, melting at 241° (uncor.). Yield, 0.099 gram.

Calculated for $\text{C}_9\text{H}_7\text{N}_3$: N, 26.76. Found: N, 26.33.

This result is fairly good considering the very small amount available for analysis.

3. By the action of heat on 3,4-diacetaminobenzonitrile.—By carefully heating the diacetaminonitrile, it loses acetic acid in the vicinity of 240°, as before mentioned, and from the residue there was isolated a substance, crystallizing from water in granules and melting at 241° (uncor.).

Calculated for $\text{C}_9\text{H}_7\text{N}_3$: C, 68.75; H, 4.49; N, 26.76.

Found: C, 68.19; H, 4.63; N, 26.55.

The imidazole, as prepared by the above methods, is usually in dull granular clusters of microscopic crystals, or occasionally in opaque needles. It sublimes as a glistening, tinsel-like deposit, and is readily soluble in acetone, glacial acetic acid, boiling water or amyl acetate; moderately soluble in alcohol; difficultly soluble in ether or chloroform; and apparently insoluble in carbon tetrachloride.

Carbamido-α-methylbenzimidazole, $\text{H}_2\text{NCO.C}_6\text{H}_3 \begin{array}{l} \diagup \text{NH} \\ \diagdown \text{N} \end{array} \text{C.CH}_3$. — As

Hübner¹ succeeded in obtaining methylbenzimidazole from *o*-nitroacetanilide by reduction with tin and glacial acetic acid, we tried the same reducing agents on the nitroacetaminobenzonitrile, except that we found the reduction to proceed apparently more efficiently with a diluted acid instead of the glacial. After heating for nine and a quarter hours with the reducing agents, the mixture was cooled and filtered, and the

¹ *Ann.*, 209, 353 (1881).

red filtrate made slightly alkaline with potassium hydroxide. A small amount of dark precipitate separated and was removed. The filtrate was treated carefully with acetic anhydride, and a nearly colorless crystalline substance separated, soluble in excess of acetic anhydride. Recrystallized twice from water, after treatment with bone-black, and then twice from alcohol, it formed colorless needles, decomposing at about 270° (uncor.). Heated with concentrated potassium hydroxide solution, ammonia was evolved.

Calculated for $C_8H_9ON_3$: C, 61.68; H, 5.18; N, 24.00.

Found: C, 61.70; H, 4.53; N, 24.44, 24.57.

These results, although the hydrogen and nitrogen figures are rather wide of the mark, seem to indicate that the substance is the carbamido-methylbenzimidazole. It is soluble in hot water, in alcohol or glacial acetic acid; and difficultly soluble or insoluble in ether, chloroform or benzene.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE ACTION OF IODIDES ON BROMANIL. IODANIL AND SOME OF ITS DERIVATIVES.¹

BY H. A. TORREY AND W. H. HUNTER.

Received March 18, 1912.

The work described in this paper was started with the intention of preparing some tetrahalogen derivatives of benzoquinone, having both bromine and iodine in the molecule, and studying the reactivity of the different halogens.² Data have been collected along two main lines: the study of the products of the reaction between potassium or sodium iodide and bromanil, and a preliminary study of the hitherto unknown iodanil. Use was made of both potassium and sodium iodide to effect the replacement of bromine by iodine, and both ethyl alcohol and acetone were used as solvents. Our use both of sodium iodide and of acetone was quite independent of the work of Finkelstein,³ and as a matter of fact antedated its publication.

The addition of solid potassium iodide to a cold acetone solution of pure bromanil resulted in the setting free of iodine, and the formation of a green compound, which was rapidly destroyed if the solution was

¹ The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy by William Hammett Hunter.

This research was suggested by the late Professor H. A. Torrey, and the experimental work was carried on under his direction, but the writing of the paper was deprived of the benefit of his supervision by his too early death.—C. L. JACKSON.

² Prel. notice in *Ber.*, **38**, 555 (1905).

³ *Ber.*, **43**, 1528 (1910).