

TABLE II.—EFFECT OF LIMING ON THE HUMUS AND NITROGEN CONTENTS OF SOILS FROM ADJACENT PLOTS.

Plot No.	Fertilized with	Limed half.		Unlimed half.	
		Humus. Per cent.	Nitrogen. Per cent.	Humus. Per cent.	Nitrogen. Per cent.
F4	Mineral Fertilizer.....	1.28	0.119	1.32	0.119
F5	“ “	1.38	0.121	1.42	0.129
F6	Farmyard manure.....	1.47	0.131	1.47	0.136
F8	Mineral fertilizer.....	1.37	0.126	1.41	0.126
G4	“ “	1.32	0.122	1.37	0.119
G5	“ “	1.33	0.118	1.34	0.125
G6	Farmyard manure and mineral fertilizer.....	1.39	0.126	1.42	0.131
G8	Mineral fertilizer.....	1.04	0.100	1.10	0.108
Average.....		1.32	0.120	1.36	0.124

TENNESSEE AGRICULTURAL EXPERIMENT STATION,
KNOXVILLE, TENN., March 4, 1908.

(CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY.
No. 151.)

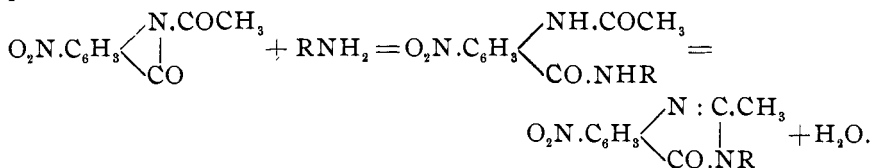
RESEARCHES ON QUINAZOLONES (TWENTIETH PAPER) ON CERTAIN 7-NITRO-2-METHYL-4-QUINAZOLONES FROM 4-NITROACETANTHRANIL.¹

BY MARSTON TAYLOR BOGERT AND WILLIAM KLABER.

Received February 28, 1908.

Bogert and Steiner² and Bogert and Seil³ have already reported on the synthesis of 7-nitro-2-methyl-4-quinazolones from 4-nitroacetanthranil and various primary amines by the Anschütz, Schmidt and Greiffenberg⁴ reaction. The present paper records the continuation and extension of this work.

The reaction involved is a simple one, and may be conveniently expressed as follows:



In one or two cases we isolated the intermediate amide.

The primary monamines used were ammonia, methyl-, *n*-propyl-, benzyl- and β -naphthylamines, aniline and *p*-anisidine. All of these

¹ Read at the General Meeting of the American Chemical Society, December 28, 1906.

² THIS JOURNAL, 27, 1327 (1905).

³ *Ibid.*, 29, 517 (1907).

⁴ *Ber.*, 35, 3480 (1902).

condensed smoothly with the acetantranil, giving good yields and clean products.

It was also found possible to condense the anthranil with amino nitriles and amino acid esters, but not with the free amino acid or its salts. Glycine ester and nitrile and anthranilic ester and nitrile were used in the experiments, and the corresponding quinazolones obtained. By the hydrolysis of the quinazolone nitriles, or by the action of ammonia upon the quinazolone esters, the corresponding amides were prepared. And from the latter, in turn, the nitriles were regenerated by the action of acetic anhydride.

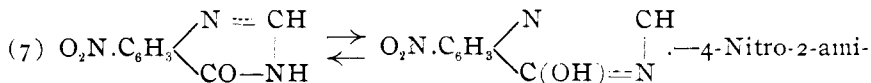
With hydrazine, both the 3-aminoquinazolone and the corresponding diquinazolonyl were obtained.¹ From the amino compound, acetyl and di-acetyl derivatives were prepared, as well as the phenylhydrazone of the monacetyl compound. By the Bülow condensation² with ethyl diaceto succinate, the pyrrole compound was produced.

7-Nitro-4-quinazolone (7-nitro-4-hydroxyquinazoline) was prepared from 4-nitro-2-aminobenzoic acid and formamide,³ and 7-amino-2-methyl-4-quinazolone by reducing the corresponding nitro compound.

Experimental.

4-Nitroacetantranil was prepared, as described by Bogert and Steiner,⁴ by nitrating *o*-toluidine in presence of excess of concentrated sulphuric acid, acetylating the 4-nitro-2-toluidine, oxidizing the nitroacetotoluidide to the nitro acetaminobenzoic acid, and converting the latter into the corresponding nitroacetantranil by the action of acetic anhydride.

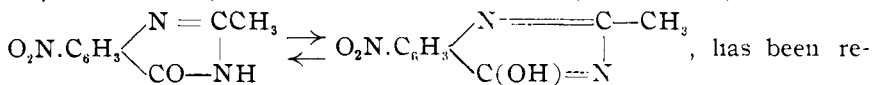
7-Nitro-4-quinazolone (7-Nitro-4-hydroxyquinazoline),



nobenzoic acid was gently fused with excess of formamide, giving a dark red solution. After removal of the excess of formamide, the residue was purified by treating with boneblack and crystallizing from alcohol. Long, slender, glistening yellow needles m. p. 276° (cor.).

Nitrogen found, 22.21. Calculated for $\text{C}_8\text{H}_5\text{O}_3\text{N}_3$: N, 22.0.

7-Nitro-2-methyl-4-quinazolone (7-Nitro-2-methyl-4-hydroxyquinazolinone),



ported previously by Bogert and Steiner⁴ and Bogert and Seil.⁴ By care-

¹ Compare Bogert and Seil, THIS JOURNAL, 28, 884 (1906); Bogert and Cook, *Ibid.*, 28, 1453 (1906).

² *Ber.*, 35, 4312 (1902); 39, 2621, 3372 (1906).

³ Nientowski, *J. prakt. Chem.* [2], 51, 564 (1895).

⁴ *Loc. cit.*

ful purification, we have succeeded in raising the melting-point from $275-7^{\circ}$ (as given by them) to $287-90^{\circ}$ (cor.). As thus purified, the substance forms silky needles of a pale greenish cast. It was prepared both from the anthranil and ammonia, and by the action of heat upon the ammonium salt of 4-nitro-2-acetaminobenzoic acid. It dissolves in neutral sodium carbonate solutions with evolution of carbon dioxide, but can be reprecipitated from this solution by saturating with carbon dioxide, as it is insoluble in the acid carbonate. It is also soluble in concentrated aqueous ammonia, but reprecipitates when the solution is boiled. It crystallizes unchanged from fused ammonium acetate. Stannous chloride reduces it to the 7-amino compound (described beyond).

Oxidation of 7-Nitro-2-methyl-4-quinazolone.—Seven grams of the quinazolone were dissolved in 300 cc. dilute sulphuric acid (one of concentrated acid to five of water) containing 14 grams chromic anhydride, and the solution boiled for about 60 hours. On cooling, small, colorless crystals separated. Dissolved in sodium carbonate solution, reprecipitated by acetic acid, and recrystallized from alcohol, colorless scales were obtained, melting at about 327° (uncor.), and dissolving with a red color in caustic or carbonated alkali solutions. Not enough of the substance was obtained for an analysis.

Potassium Salt of 7-Nitro-2-methyl-4-hydroxyquinazoline.—The quinazoline was dissolved in dilute potassium hydroxide solution and this solution then saturated with solid potassium carbonate. The yellow precipitate was filtered out, dissolved in absolute alcohol, and the filtered solution evaporated to dryness, leaving a pale yellow crystalline mass easily soluble in water or alcohol. It crystallizes from alcohol with alcohol of crystallization as a pale yellow solid, the color deepening to an orange on driving out the alcohol. It was analyzed by titration with fifth-normal sulphuric acid, using phenolphthalein as indicator.

Potassium found, 16.21. Calculated for $C_9H_8O_3N_3K$: K, 16.11.

Silver Salt.—The quinazoline was dissolved in concentrated aqueous ammonia, the solution heated to boiling, and ammoniacal silver nitrate solution added gradually as long as it gave a precipitate. The precipitate was voluminous and curdy, and of a faint yellow color. It was washed thoroughly with dilute ammonia water and dried. It is decomposed quantitatively when heated with a salt solution. Analyzed in this way, it gave the following result:

Silver found, 34.35. Calculated for $C_9H_8O_3N_3Ag$: Ag, 34.60.

7-Nitro-2,3-dimethyl-4-quinazolone, $O_2N.C_6H_3$ $\begin{cases} N : C.CH_3 \\ | \\ CO.NCH_3 \end{cases}$.—Bogert and

Steiner¹ prepared this substance by the action of methylaniline upon the

¹ *Loc. cit.*

4-nitroacetantranil. We have also obtained it by heating the methylamine salt of 4-nitroacetantranilic acid at 190–200°, but the yield by this latter method is poor and the product quite impure. It is unchanged by fusion with ammonium acetate or by heating with ammonium formate for three hours in a sealed tube at 230°. Bogert and Steiner describe the compound as forming light yellowish green crystals, m. p. 144–5° (cor.). We have succeeded in getting it nearly colorless and of a m. p. 151–2° (cor.).

7-Nitro-2-methyl-3-n-propyl-4-quinazolone, from 4-nitroacetantranil and *n*-propylamine, crystallizes from dilute alcohol in colorless needles, m. p. 140° (cor.). It is slightly soluble in water and soluble in alcohol.

Nitrogen found, 16.9. Calculated for $C_{12}H_{13}O_3N_3$: N, 17.0.

7-Nitro-2-methyl-3-phenyl-4-quinazolone, from the nitroacetantranil and aniline, crystallizes from alcohol in nearly colorless, diamond-shaped plates, m. p. 209° (cor.).

Nitrogen found, 14.82. Calculated for $C_{15}H_{11}O_3N_3$: N, 14.94.

7-Nitro-2-methyl-3-benzyl-4-quinazolone, from the nitroacetantranil and benzylamine, crystallizes from alcohol in coarse, yellowish, cubical forms, m. p. 131–2° (cor.).

Nitrogen found, 14.27. Calculated for $C_{16}H_{13}O_3N_3$: N, 14.23.

Its *hydrochloride* forms pale yellowish crystals, m. p. 229–30° (cor.), which lose their HCl when boiled with alcohol.

Nitrogen found, 12.92. Calculated for $C_{16}H_{14}O_3N_3Cl$: N, 12.67.

7-Nitro-2-methyl-3-p-anisyl-4-quinazolone, from the nitroacetantranil and *p*-anisidine, crystallizes from alcohol in glistening scales, of a faintly yellowish cast, m. p. 228° (cor.).

Nitrogen found, 13.49. Calculated for $C_{16}H_{13}O_4N_3$: N, 13.50.

7-Nitro-2-methyl-3-β-naphthyl-4-quinazolone, from the nitroacetantranil and β-naphthylamine. Fine, colorless needles (from alcohol), m. p. 218–9° (cor.).

Nitrogen found, 12.64. Calculated for $C_{19}H_{13}O_3N_3$: N, 12.68.

7-Amino-2-methyl-4-quinazolone (*7-amino-2-methyl-4-hydroxyquinazoline*).—The 7-nitro compound was reduced with stannous chloride and hydrochloric acid. The double chloride of tin and the amino quinazoline which separated was boiled with dilute sodium carbonate solution and filtered hot. On cooling, the 7-aminoquinazoline separated from the filtrate in long, silky, colorless needles, m. p. 311° (cor.), identical with the quinazoline obtained by the action of potassium hydroxide solution upon 7-acetamino-2-methyl-4-quinazolone (which will be described in another paper). It is soluble in hot water, alcohol or caustic alkali solutions, but not in cold sodium carbonate solutions. Crystals obtained from water or alcohol carry approximately half a molecule of the solvent.

Nitrogen found, 24.22. Calculated for $C_9H_9ON_3$: N, 24.0.

7-Nitro-2-methyl-3-amino-4-quinazolone. — 4-Nitroacetanthranil was added gradually to an excess of 50 per cent. hydrazine hydrate solution (aqueous). Considerable heat was developed and the reaction was completed by further final warming. When cold, the insoluble product was extracted with a small amount of alcohol, to remove nitroanthranilic acid and small amounts of impurities, and the residue was then purified by crystallization from alcohol. Shining, pale yellow needles, m. p. 223° (cor.). With acetic anhydride it gives both mono- and diacetyl derivatives.

Nitrogen found, 25.73 and 25.74. Calculated for $C_9H_8O_3N_4$: N, 25.45.

The yield of pure aminoquinazolone was generally about 50 per cent. of the theory.

7-Nitro-2-methyl-3-amino-4-quinazolone and phenylhydrazine. — The amino quinazolone was mixed with excess of phenylhydrazine and the mixture heated just to boiling. As soon as ebullition began, the flame was removed, as considerable heat is developed by the reaction. Ammonia was evolved. When the action moderated, the heating was renewed for a short time, the mass allowed to cool somewhat, excess of acetic acid added and the mixture warmed up again. This second phase of the reaction also proceeds with considerable rise of temperature, due to the combination of the acetic acid with the excess of phenylhydrazine and the formation of acetylphenylhydrazide, and the flame should be removed as soon as the reaction threatens to become violent. The dark colored product is heated for a short time further, concentrated to small volume and allowed to crystallize. The mixture is diluted largely with cold water, the insoluble material crystallized from alcohol and washed with ether. From very dilute potassium hydroxide solution it separated in fine needles, which were recrystallized from alcohol, giving clusters of colorless, feathery needles, m. p. 230° (uncor.), insoluble in ether, soluble in hot water, easily soluble in alcohol.

Found: C, 48.62 and 48.82; H, 5.9 and 5.52; N, 25.60 and 25.54.

These figures are far removed from those calculated for the phenylhydrazinoquinazolone, the phenylhydrazinophenylhydrazone, or the osotetrazole which might be formed from the latter by loss of a molecule of aniline. The compound has not been identified.

A similar product was obtained by heating the amino quinazolone with two molecules of phenylhydrazine in cumene solution, water and ammonia being evolved. When the heating was conducted in nitrobenzene or alcoholic acetic acid solution, but little action took place.

7-Nitro-2-methyl-3-acetamino-4-quinazolone. — The above quinazolone, when heated with acetic anhydride, gave a clear solution. This solution was concentrated to crystals, which were washed with carbon tetrachloride and recrystallized from benzene. Short, colorless prisms, m.

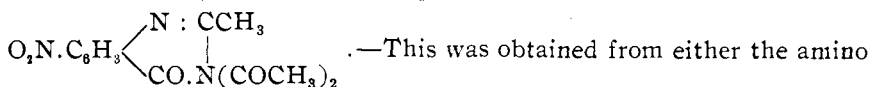
p. 233° (cor.), soluble in alcohol, insoluble in carbon tetrachloride, and but sparingly soluble in cold benzene.

Nitrogen found, 21.49. Calculated for $C_{11}H_{10}O_4N_4$: N, 21.37.

Phenylhydrazone.—The acetaminoquinazolone and phenylhydrazine were heated just to boiling and the flame removed. If large amounts are used, the reaction proceeds with considerable violence and frothing. On cooling, the mass solidified. It was washed with ether and crystallized from alcohol. Beautiful, glassy prisms, m. p. 315° (cor.).

Found: C, 57.80; H, 4.90; N, 23.4. Calculated for $C_{17}H_{16}O_3N_6$: C, 57.95; H, 4.54; N, 23.86.

7-Nitro-2-methyl-3-diacetamino-4-quinazolone,

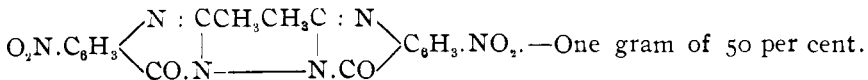


or acetaminoquinazolone by the further action of acetic anhydride. The diacetyl compound is much more soluble in benzene than the monacetyl and the two can be separated in this way. The diacetyl derivative was separated from the benzene mother liquors by careful addition of gasoline. It crystallizes in pale yellow, glassy plates, m. p. 132° (cor.), soluble in alcohol, benzene, or acetic anhydride. Oxidation with neutral permanganate yielded only 4-nitroanthranilic acid and its acetyl derivative.

Nitrogen found, 18.79 and 18.89. Calculated for $C_{13}H_{12}O_5N_4$: N, 18.42.

When the diacetyl derivative was boiled with phenylhydrazine in alcoholic acetic acid solution, the only change noted was the formation of the monacetyl compound. No hydrazone was observed. A boiling alcoholic solution of aniline had the same effect in changing the diacetyl to the monacetyl derivative.

7,7'-Dinitro-2,2'-dimethyl-4,4'-diketotetrahydro-3,3'-diquinazolyl,



aqueous hydrazine hydrate solution was added to 6.4 grams 4-nitroacetanthranil and the mixture heated for a short time on the sand-bath. When cold, the solid product was extracted with dilute acetic acid, to remove aminoquinazolone, and the residue crystallized from a mixture of ethyl and isoamyl acetates. Small, yellow, granular crystals, m. p. 337.5° (cor.). The yield was poor.

Nitrogen found, 20.63. Calculated for $C_{18}H_{12}O_6N_6$: N, 20.58.

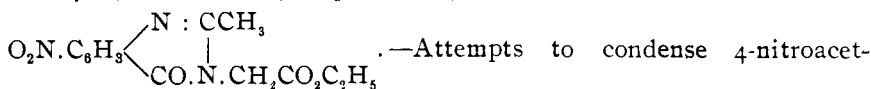
The substance is soluble in ethyl or isoamyl acetates, but is insoluble in water, alcohol, and in the majority of the ordinary organic solvents. It dissolves in acetic anhydride and, on cooling, white crystals separate,

m. p. 227° (uncor.). probably similar to the acetic anhydride addition-product described by Bogert and Seil¹ for the corresponding 5,5'-dinitro-diquinazolyl.

4-Nitroacetanthranil and Guanidine.—When these substances were heated together in aqueous solution, in equal molecules, the guanidine salt of 4-nitroacetanthranilic acid was obtained. It forms coarse, lentil-shaped crystals, m. p. 247° (cor.).

In one case, where two molecules of the anthranil were used to one of the guanidine, a small amount of a yellow substance was isolated, which melted sharply at 253°, resolidified and did not re-melt below 300°. It was not obtained in sufficient amount to identify.

Ethyl 7-Nitro-2-methyl-4-quinazolonyl-3-acetate,



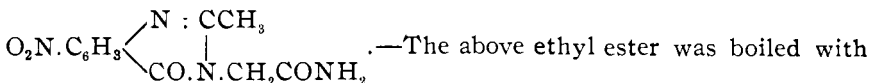
anthranil with free glycine or with its sodium salt failed. Heating with aqueous solutions caused only hydrolysis of the anthranil, while direct dry heating resulted in decomposition.

Three and one-half grams glycine ester hydrochloride were dissolved in the smallest possible amount of water and the hydrochloric acid removed by the addition of the moist silver oxide from 4.66 grams of silver nitrate. Five grams of the anthranil were then added to the mixture, and the temperature raised rapidly to the boiling-point. The close of the reaction was indicated by the clearing of the solution, followed by the appearance of turbidity in the supernatant liquid. The quinazolone ester was extracted with ether and purified by crystallization from the same solvent. Asbestos-like sheaves of colorless crystals, m. p. 139–40° (cor.).

Nitrogen found, 14.38. Calculated for $\text{C}_{13}\text{H}_{13}\text{O}_5\text{N}_3$: N, 14.43.

After the ether extraction, the residual solution was found to contain some nitroacetanthranilic acid.

7-Nitro-2-methyl-4-quinazolonyl-3-acetamide,



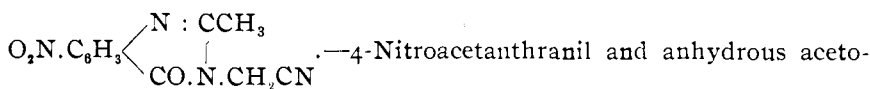
excess of concentrated aqueous ammonia until a clear solution was obtained. On cooling, colorless, very fine, silky needles separated. Recrystallized from alcohol, they showed a m. p. of 275° (cor.).

Nitrogen found, 21.45. Calculated for $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_4$: N, 21.37.

When boiled with acetic anhydride, it gave the nitrile described below.

7-Nitro-2-methyl-4-quinazolonyl-3-acetonitrile,

¹ THIS JOURNAL, 28, 892 (1906).



nitrile were found to be without action upon each other at the boiling-point of the nitrile (81°) or in a sealed tube at 160°.

4.17 grams potassium hydroxide were dissolved in a small amount of water, the solution cooled in an ice pack, and 5.78 grams aminoacetone-trile sulphate (50 per cent. excess) added slowly with stirring, care being taken to prevent any considerable rise of temperature. Five grams nitroacetanthranil were then quickly stirred in and the mixture heated rapidly to boiling. After boiling for about five minutes, the dark red solution was allowed to cool, cold water added, the mixture thoroughly stirred, and the precipitate filtered out. This was treated with bone-black in acetone solution, and repeatedly crystallized from the same solvent. Colorless, shining scales, m. p. 207–8° (cor.), insoluble in water or petroleum distillates, soluble in alcohol, acetone or dilute acetic acid.

Nitrogen found, 23.10. Calculated for $\text{C}_{11}\text{H}_8\text{O}_3\text{N}_4$: N, 22.90.

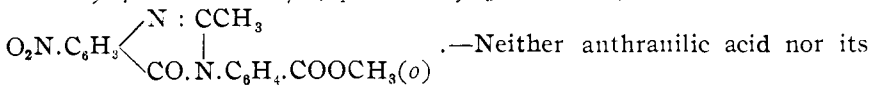
4-Nitro-2-acetaminohippuronitrile.

(4) $\text{O}_2\text{N}(2)\text{CH}_3\text{CONH} \cdot \text{C}_6\text{H}_3 \cdot \text{CONHCH}_2\text{CN}$.—This intermediate amide was found in the acetone mother liquors from the above quinazolone. It is very much more soluble in acetone than the quinazolone and can be separated by this property. It crystallizes in colorless prisms, melting with effervescence at 194° (cor.) (probably changing to the quinazolone), and is readily changed to the quinazolone by heating with very dilute potassium hydroxide solution.

Nitrogen found, 21.53. Calculated for $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_4$: N, 21.37.

When ethyl β -aminocrotonate and 4-nitroacetanthranil were heated together, only 7-nitro-2-methyl-4-quinazolone (7-nitro-2-methyl-4-hydroxyquinazoline) was obtained. This is, of course, due to the fact that the aminocrotonic ester loses ammonia very readily, and this ammonia then condenses with the anthranil to the simple quinazolone.

Methyl 7-Nitro-2-methyl-4-quinazolonyl-3-o-benzoate,

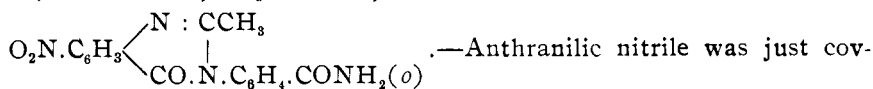


sodium salt could be made to condense with 4-nitroacetanthranil.

The anthranil was heated for a short time with excess of methyl anthranilate and the mixture then allowed to cool. The resultant glassy solid was extracted with alcohol, the alcoholic solution treated with bone-black, and the precipitate which separated on cooling treated with cold dilute potassium hydroxide solution, to remove nitroacetanthranilic acid. The residue, crystallized from alcohol, gave canary-yellow, granular crystals, m. p. 175° (cor.), quite soluble in alcohol, but insoluble in

Nitrogen found, 12.52. Calculated for $C_{17}H_{13}O_5N_3$: N, 12.38.

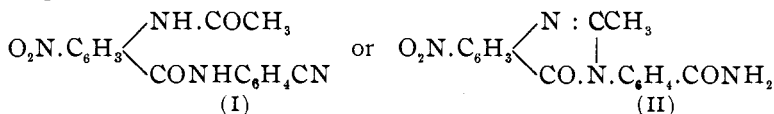
7-Nitro-2-methyl-4-quinazolonyl-3-o-benzamide,



with water and the mixture heated to boiling. The nitrile remained largely undissolved as a yellow oil. 4-Nitroacetanthranil was then added. The oily nitrile turned dark and finally solidified to a yellow mass, a precipitate also appearing in the supernatant liquid. Potassium carbonate was added to the cold solution, to remove nitroacetanthranilic acid. The residue was then extracted with ethyl acetate, to eliminate certain easily soluble impurities, and the undissolved portion crystallized from nitrobenzene, the excess of solvent being washed out with alcohol. Straw-colored needles, m. p. $320-1^\circ$ (cor.), soluble in nitrobenzene or acetic anhydride but only moderately soluble in alcohol.

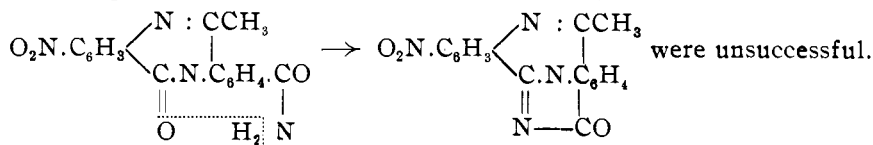
Nitrogen found, 17.34, 17.28 and 17.38. Calculated for $C_{16}H_{12}O_4N_4$: N, 17.3.

The product might have either of the following structures:

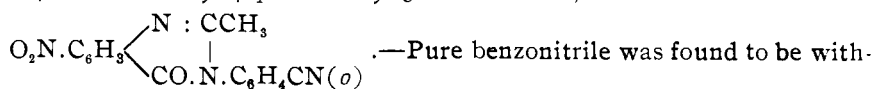


Boiled with acetic anhydride, it gave the benzonitrile quinazolone described below, from which it can also be produced by five to six hours' boiling with alcohol, the conversion being a quantitative one. This dehydration could occur quite readily with either structure, but the easy re-hydration of the benzonitrile quinazolone to the same product would seem to us to exclude formula (I). Further, the compound does not melt and re-solidify below the m. p. of the quinazolone, as is usually the case with such intermediate amides as (I), nor does it change to the quinazolone on long boiling in nitrobenzene as (I) might be expected to do in line with the synthesis of the benzonitrile quinazolone described below.

Attempts to bring about a further condensation, thus:



7-Nitro-2-methyl-4-quinazolonyl-3-o-benzonitrile,



action upon 4-nitroacetanthranil.

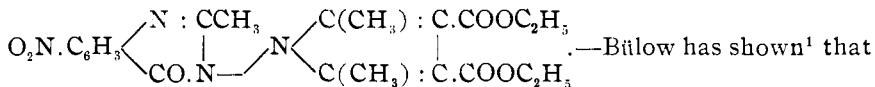
By fusing anthranilic nitrile with the nitroacetanthranil, and extracting the product with ether, heavy red needles were obtained, m. p. 225° (uncor.).

In a second experiment, the condensation was carried out in boiling nitrobenzene solution. The reddish crystals were treated with bone-black in benzene solution, and recrystallized from alcohol. Slender, glistening, yellowish needles, m. p. 234° (cor.); soluble in alcohol, benzene, ether, nitrobenzene or acetic anhydride.

Nitrogen found, 18.23 and 18.45. Calculated for $C_{10}H_{10}O_3N_4$: N, 18.30.

Long boiling with 95 per cent. alcohol changed this compound completely to the amide mentioned above, from which it could, as stated, be regenerated by dehydration with acetic anhydride. As anthranilic nitrile itself is rather resistant to hydrolysis, the ease with which this quinazolone nitrile changes to the amide is rather surprising.

7-Nitro-2-methyl-4-quinazolonyl-3-(2,5-dimethyl-3,4-dicarbethoxy pyrrole),



hydrazines of the type $RNHNH_2$ or R_2NNH_2 condense with diacetosuccinic ester to derivatives of pyrrole.

Three grams of the 3-aminoquinazolone and four of ethyl diacetosuccinate were dissolved in 40 cc. of glacial acetic acid, the solution boiled for three hours, and then concentrated. A small amount of precipitate separated on cooling. This was removed, and alcohol added to the mother liquor. A white precipitate resulted, which was purified by repeated crystallization from alcohol, until it appeared in colorless, shining, minute scales, of a constant m. p. of 171° (cor.).

Found: C, 56.45; H, 4.8; N, 12.86. Calculated for $C_{21}H_{22}O_7N_4$: C, 57.0; H, 4.97; N, 12.67.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
NEW YORK, February 25, 1908.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

ON THE ACTION OF α -BENZOYLPHENYLHYDRAZINE ON THE HALOGEN DERIVATIVES OF QUINONES,

BY WILLIAM MCPHERSON AND WILBUR L. DUBOIS.

Received March 26, 1908.

The action of phenylhydrazine on quinones was first investigated by Zincke.² He showed that phenylhydrazine, as well as its salts, acted

¹ *Loc. cit.*

² *Ber.*, 16, 1563.