was heated with a slight excess of benzaldehyde for an hour at 180°, but no condensation occurred.

The reaction is of interest, since we have shown that amino groups in positions 3 or 7 condense easily with benzaldehyde.

2-Methyl-4-quinazolone and Ethyl Oxalate.—Five grams of the dry quinazolone, a similar amount of ethyl oxalate, and 2 grams finely pulverized sodium ethylate, together with 100 cc. anhydrous ether, were placed in a well-stoppered flask and left at the laboratory temperature for three weeks, with occasional shaking. No condensation occurred, the quinazolone being recovered unchanged.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 203.]

RESEARCHES ON QUINAZOLINES (THIRTIETH PAPER). A STUDY OF THE BROMINATION AND NITRATION OF 4-QUINAZOLONES; THE CORRESPONDING AMINOQUINAZOLONES, AND CERTAIN OTHER NEW 4-QUINAZOLONES.[1]

BY MARSTON TAYLOR BOGERT AND GEORGE AUGUSTUS GEIGER.

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The 4-quinazolones (4-hydroxyquinazolines) are not easily brominated by the action of bromine in aqueous potassium bromide solution, in glacial acetic acid or in acetic anhydride solution. By employing the Juvalta[2] process, however, the halogen may be introduced. In this way, monobromo derivatives have been obtained of 4-quinazolone and of 2-methyl-4-quinazolone.

Nor are the quinazolones readily nitrated. Griess,[3] in 1869, showed that benzoylene urea could be nitrated, but did not prove the position of the nitro group. In 1890, Dehoff[4] nitrated 2-methyl and 2,3-dimethyl-4-quinazolone, and his products were subsequently shown to be the 6-nitro derivatives by the investigations of Thieme[5] and of Bogert and Cook.[6]

According to our experience, the satisfactory nitration of 4-quinazolones requires a high temperature and the use of a mixture of fuming nitric and concentrated sulfuric acids, and but one nitro group can thus be introduced on the 4-quinazolone nucleus. Position 6 seems to be the point where the nitro group enters most readily. Of course, aryl

[1] Read at the Washington Meeting of the Society, Dec. 29, 1911.
[2] D. R. P. 50,177, *Friedländer*, **2**, 93.
[3] *Ber.*, **2**, 416 (1869).
[4] *J. prakt. Chem.*, [2] **42**, 347 (1890).
[5] Thieme, *Ibid.*, **43**, 473 (1891).
[6] THIS JOURNAL, **28**, 1449 (1906).

radicals attached to the quinazoline nucleus, at positions 2 or 3, for example, may also be nitrated in the reaction.

Nitration of the following gives mononitro derivatives: 4-quinazolone, 3-methyl-4-quinazolone, 3-ethyl-4-quinazolone and 2-methyl-3-ethyl-4-quinazolone. With 2-methyl-3-phenyl-4-quinazolone, a dinitro derivative results which is not identical with the dinitro compound obtained by nitrating 2-methyl-3-*p*-nitrophenyl-4-quinazolone. A dinitro derivative is also obtained from 2-methyl-3-*p*-tolyl-4-quinazolone.

The action of nitric acid upon 2-methyl-4-quinazolone, in presence of metallic mercury, gives only the mercury salt of the quinazolone, whereas with benzene dinitrophenol results, and with quinoline both an hydroxyl and nitro group are simultaneously introduced on the benzene portion of the molecule.[1]

Griess[2] showed that nitro benzoylene urea could be reduced to the amino compound. Bogert and Chambers[3] have prepared 5-amino-4-quinazolone, and Bogert and Klaber[4] 7-amino-4-quinazolone, by reduction of the corresponding nitro compounds. Zacharias[5] reduced 8-nitro-2-methyl-4-quinazolone, but failed to get a pure product. Dehoff[2] also failed in his attempt to reduce the 6-nitro-2-methyl-4-quinazolone.

Although the yields were generally poor, we have experienced no particular difficulty in reducing the 6-nitro-4-quinazolones to the corresponding amines, including the 6-nitro-2-methyl-4-quinazolone.

The new amino derivatives so prepared are as follows: amino and acetamino 4-quinazolone, amino and acetamino 3-methyl-4-quinazolone, 6-amino-2,3-dimethyl-4-quinazolone and 6-amino-2-methyl-3-ethyl-4-quinazolone.

In the prosecution of the research, the following new 4-quinazolones were also prepared: 3-ethyl, 3-benzyl-2-methyl-3-*p*-nitrophenyl, 2-methyl-3-*p*-tolyl, 2-methyl-3-α-naphthyl and 2-methyl-3-β-naphthyl.

Incidentally, it was found that the melting point of 71° assigned by Knape[6] to 3-methyl-4-quinazolone is really that of the hydrated form, the anhydrous compound melting at 105° (cor.).

Experimental.

I. Simple 4-Quinazolones.

3-Methyl-4-quinazolone, HC : $N.C_6H_4.CO.N.CH_3$, was prepared first by Knape,[3] by direct methylation of 4-quinazolone with potassium hydroxide and methyl iodide in methyl alcohol solution. The author states that

[1] Wolffenstein and Boeters, D. R. P. 214,045.

[2] *Loc. cit.*

[3] THIS JOURNAL, **28**, 207 (1906).

[4] *Ibid.*, **30**, 807 (1908).

[5] *J. prakt. Chem.*, [2] **43**, 443 (1891).

[6] *Ibid.*, [2] **43**, 216 (1891).

the crude product, washed with methyl alcohol and recrystallized from chloroform or ligroin, gave long needles of satiny luster, melting at 71°.

On repeating this process, and crystallizing the crude product from chloroform, we obtained colorless crystals, melting at 105° (cor.). This proved to be the pure anhydrous compound. When this quinazolone is crystallized from water, it carries a molecule of water of crystallization, and then melts at 71°, the point given by Knape.

The most convenient method of preparing the substance is to dissolve the 4-quinazolone in methyl alcohol containing the calculated amount of potassium hydroxide, add the required amount of methyl iodide, and let the mixture stand at laboratory temperature. In one and a half to two hours the solution changes to a mass of colorless crystals, which are filtered out and dissolved in the minimum amount of cold water. In about 15 minutes, the crystals separate again, and are then recrystallized from hot water, giving colorless needles, melting at 70–1° (cor.).

These were dried in vacuum over concentrated sulfuric acid for four days, then heated at 80° for an hour, and again dried in vacuum for an hour:

Calculated for $C_9H_8ON_2.H_2O$: H_2O, 10.1. Found: H_2O, 10.0.

The dehydrated substance then melted at 105° (cor.). It was analyzed with the following result:

Calculated for $C_9H_8ON_2$: N, 17.50. Found: N, 17.32.

2,3-Dimethyl-4-quinazolone[1] also crystallizes from water with a molecule of water of crystallization, and it is interesting that the melting points of its hydrated and anhydrous forms are almost identical with those of the above 3-methyl compound:

3-Methyl, m. p. of hydrated form 70–1°; anhydrous m. p. 105°.

2,3-Dimethyl, m. p. of hydrated form 70°; anhydrous m. p. 107–9°.

A mixture of the anhydrous forms of the two substances melts at 78–9°.

3-Ethyl-4-quinazolone.—20 grams 4-quinazolone were placed in a flask, sufficient ethyl alcohol added to make a thick paste, and then 7.6 g. solid potassium hydroxide. The flask was shaken until all the quinazolone had dissolved, 21 g. ethyl iodide poured in, and the mixture boiled under a return condenser until it showed a neutral reaction (about three-quarters of an hour). The alcohol was then distilled off, leaving a mass of potassium iodide crystals and a viscous liquid. This residue dissolved completely in 100 cc. cold water. As a previous experiment had shown that nothing could be separated from this aqueous solution by distillation with steam, it was extracted repeatedly with ether, adding some salt to the aqueous solution after the first extraction. The ether extracts were combined, dried with potassium carbonate (calcium chloride gives a yellower product), and the ether driven off, leaving the quinazolone as

[1] Weddige, *J. prakt. Chem.*, [2] 36, 147 (1887).

a crystallin mass. By careful recrystallization from ether, it was obtained in colorless needles, melting at 102° (cor.). Yield, 54% (13 g.). It may also be purified by distillation under reduced pressure (b. p. at 15 mm., 182°), when it comes over as a colorless oil, solidifying on cooling.

The pure compound dissolves also in water, alcohol, acetone or benzene, but does not crystallize well from any of these solvents.

Calculated for $C_{10}H_{10}ON_2$: N, 16.09. Found: N, 16.06.

3-Benzyl-4-quinazolone was prepared in similar manner from 4-quinazolone, methyl alcohol, potassium hydroxide and benzyl chloride. The reaction product was filtered hot from potassium chloride, and the desired quinazolone crystallized from the filtrate in colorless needles, which were washed with boiling water and recrystallized from dilute methyl alcohol, giving long, glassy needles, melting at 116° (cor.). Yield, 6 g. from 10 g. of quinazolone.

Calculated for $C_{15}H_{12}ON_2$: C, 76.27; H, 5.08; N, 11.86. Found: C, 76.08; H, 4.82; N, 11.98.

It is difficultly soluble in chloroform, benzene, acetone or alcohol, when cold, but dissolves in these solvents at their boiling points. It is but slightly soluble in ether.

2-Methyl-3-p-nitrophenyl-4-quinazolone, $CH_3.C{:}N.C_6H_4.CO.N.C_6H_4.NO_2$. —An intimate mixture of 4 g. acetanthranil and 3 g. *p*-nitraniline was heated for three-quarters of an hour at 190°. The gummy melt solidified on cooling. On repeated crystallization of this mass from alcohol, glistening, pale yellowish scales were obtained, melting at 193° (cor.). Yield, 2 g.

Calculated for $C_{15}H_{11}O_3N_3$: C, 64.05; H, 3.91; N, 14.94. Found: C, 63.81; H, 4.00; N, 15.04.

When *m*-nitraniline was used instead of the para compound, the desired quinazolone was not obtained.

2-Methyl-3-p-tolyl-4-quinazolone.—An intimate mixture of 10 g. acetanthranil and 7 g. *p*-toluidine was carefully heated. At about 80°, the mass began to melt, and at 100° steam was evolved. The temperature of the bath was slowly raised to 135° and kept there for half an hour. The melt was crystallized from dilute alcohol until pure, when it appeared in small, glistening, pale yellow scales, melting at 151° (cor.); soluble in benzene, acetone, chloroform or methyl alcohol, less readily in ether. Yield, 10 g.; or about 66% of theory.

Calculated for $C_{16}H_{14}ON_2$: N, 11.20. Found: N, 11.37.

2-Methyl-3-α-naphthyl-4-quinazolone.—An intimate mixture of acetanthranil and α-naphthylamine was heated gradually to 150°, and the temperature held at that point for about an hour. The resultant melt was poured while warm into excess of alcohol, the alcoholic solution pre-

cipitated by careful dilution with water, and the precipitate recrystallized from dilute alcohol. Small, nearly colorless plates were obtained, melting at 136° (cor.), which possessed an odor resembling that of α-naphthylamine, possibly due to a trace of this substance, and which turned a pale pink on standing in the air. Yield, 10.5 g. The compound is soluble in acetone, chloroform or benzene, and less easily in ether.

Calculated for $C_{19}H_{14}ON_2$: N, 9.79. Found: N, 9.82.

2-Methyl-3-β-naphthyl-4-quinazolone, prepared in practically the same way, crystallizes from alcohol in nodules of short needles, of a pinkish cast, melting at 175° (cor.), and is less soluble in alcohol than the α-compound.

Calculated for $C_{19}H_{14}ON_2$: N, 9.79. Found: N, 9.91.

II. Bromination of 4-Quinazolones.

Monobromo-4-quinazolone, $\begin{matrix}\ulcorner\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\urcorner\\ HC : N.C_6H_3Br.CO.NH.\end{matrix}$—Attempts to brominate 4-quinazolone with a solution of bromine in aqueous potassium bromide, or by bromine in acetic acid solution, all failed. The Juvalta[1] process was therefore applied.

Two grams of the quinazolone were dissolved in 60 cc. fuming sulfuric acid and 2 cc. bromine gradually added. The temperature was raised slowly to 115° and kept there for an hour and a half. When cold, the solution was partly neutralized with solid sodium carbonate and then poured into about 300 cc. ice water. A brownish precipitate separated. It was filtered out, dissolved in dilute alcohol, the hot solution decolorized with bone-black and filtered. From the filtrate, on cooling, there separated a colorless flocculent mass, which was further purified by dissolving it in dilute potassium hydroxide solution and reprecipitating with acetic acid.

Calculated for $C_8H_3ON_2Br$: N, 12.44; Br, 35.55. Found: N, 12.28; Br, 35.79.

The compound melts at 258° (uncor.). It is soluble in acetone, methyl or ethyl alcohols; insoluble or difficultly soluble in water, benzene, ether or chloroform.

Monobromo-2-methyl-4-quinazolone, $\begin{matrix}\ulcorner\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\urcorner\\ CH_3C : N.C_6H_3Br.CO.NH.\end{matrix}$—Addition of bromine to the quinazolone in glacial acetic acid or acetic anhydride solution yielded what was apparently only the hydrobromide of the original substance, since on dissolving it in dilute potassium hydroxide solution and reprecipitating with carbon dioxide, the quinazolone was recovered. Similar results were recorded when the quinazolone was triturated in a mortar to a thick paste with a solution of bromine in aqueous potassium bromide and the paste then dried at 110°.

In this case also, it was necessary finally to resort to the Juvalta method,

[1] *Loc. cit.*

as described for the 4-quinazolone itself, the reaction being carried out in a similar manner. The product obtained by dissolving the crude substance in dilute potassium hydroxide solution and precipitating with acetic acid was colorless and gelatinous. Dried at 110°, it melted at 277° (uncor.). Yield, 55%.

Calculated for $C_8H_7ON_2Br$: N, 11.71; Br, 33.47. Found: N, 11.73; Br, 33.99.

It is moderately soluble in cold methyl alcohol, soluble in hot acetone, insoluble in ether or benzene.

III. Nitration of 4-Quinazolones.

Mononitro-4-quinazolone, $HC : N.C_6H_3(NO_2).CO.NH$.—Fuming nitric acid (sp. gr. 1.6) alone failed to nitrate the quinazolone.

Five grams of the quinazolone were added carefully to a mixture of 10 cc. concentrated sulfuric and 10 cc. fuming (sp. gr. 1.6) nitric acids, the solution concentrated to half its volume, cooled, and poured into 500 cc. ice water. The nitro derivative separated in beautiful, silky, yellow plates. Washed with water, the compound lost its crystalline character and became granular and pulverulent. It was further purified by solution in sodium hydroxide and reprecipitation with acetic acid. As thus purified, it forms a practically colorless powder, darkening slightly at about 275°, and melting with decomposition at 284° (uncor.). Yield, 60%.

Calculated for $C_8H_5O_3N_3$: N, 21.99. Found: N, 21.63, 22.15.

It is moderately soluble in hot water, and in methyl or ethyl alcohol; insoluble or difficultly soluble in benzene, ether or chloroform. It dissolves in dilute sodium hydroxide solution to a yellow or reddish solution depending upon the concentration. With sodium hydroxide and methyl iodide, it gives the 3-methyl derivative. Its nitro group is very probably at position 6.

6-Nitro-2-methyl-4-quinazolone, $CH_3.C : N.C_6H_3(NO_2).CO.NH$. — Five grams of the quinazolone were added gradually to 25 cc. fuming nitric acid (sp. gr. 1.52) and the solution then concentrated to half its volume. When cold, the solution was poured into 50 cc. ice water, and the precipitated nitro-quinazolone purified by crystallization from dilute alcohol, or by dissolving in dilute sodium hydroxide solution and reprecipitating with carbon dioxide or acetic acid.[1] Yield, 66%. The pure substance forms pale yellow needles which begin to decompose at about 266° and melt at 299° (uncor.). Small amounts of impurities depress this melting point considerably, and the figure 278–81° given by Bogert and Cook[2] was obtained on an insufficiently purified sample, as we have proven by

[1] Dehoff, *Loc. cit.*

[2] *Loc. cit.*

examining their original material, further purification of which raised its melting point to 299°.

When this compound is heated with concentrated hydrochloric acid in a sealed tube at 250°, decomposition and charring result.

The influence of the presence of metallic mercury in the above nitration was also investigated. The interaction of the quinazolone, fuming nitric acid (sp. gr. 1.4 or 1.5) and metallic mercury, irrespective of the order in which they were mixed, invariably yielded a dark mass which when poured into cold water gave a yellow to brownish precipitate, insoluble in dilute aqueous caustic alkalies, alcoholic alkali, benzene, nitrobenzene, aniline, ether, chloroform, toluene, amyl alcohol or amyl acetate; but soluble in hot, glacial acetic acid or in mineral acids. Neutralization of the acetic acid solution by sodium hydroxide yielded a yellow gelatinous precipitate, which crystallized from glacial acetic acid as a yellow powder, melting above 360°, and proved to be the mercury salt of the original unnitrated quinazolone:

Calculated for $C_9H_7ON_2Hg$: N, 7.79. Found: N, 7.85. The presence of mercury in the compound was demonstrated qualitatively.

Mononitro-3-methyl-4-quinazolone, $HC : N.C_6H_3(NO_2).CO.N.CH_3$. — A mixture of 5 g. nitro-4-quinazolone and 125 cc. methyl alcohol, with the calculated amounts of potassium hydroxide and methyl iodide, was boiled gently for two hours under a reflux condenser. On cooling, the methyl derivative crystallized out. Recrystallized from methyl alcohol, it was obtained in colorless crystals, melting at 196° (cor.).

The same substance was obtained by nitrating 5 g. of anhydrous 3-methyl-4-quinazolone with 20 cc. of a mixture consisting of one-third concentrated sulfuric and two-thirds fuming nitric (sp. gr. 1.6) acids, evaporating to one-third the original volume, cooling, pouring upon ice, and recrystallizing the crude product from water. Yield, about 70%. When pure, the substance is nearly colorless. It is soluble in water, alcohol, acetone or benzene, but not appreciably soluble in ether.

Calculated for $C_9H_7O_3N_3$: N, 20.48. Found: N, 20.64.

Mononitro-3-ethyl-4-quinazolone, $HC : N.C_6H_3(NO_2).CO.N.C_2H_5$.—Two grams of 3-ethyl-4-quinazolone were added to a mixture of 5 cc. concentrated sulfuric and 15 cc. fuming (sp. gr. 1.52) nitric acids and the whole boiled down to about half its volume, cooled, and poured upon ice. Fine, colorless needles separated which became pulverulent when washed with water. Recrystallized from water, it was obtained in colorless, thin needles, melting at 165° (cor.). Yield, 1.2 g. (47%). It is also soluble in alcohol. The nitro group is most probably at position 6.

Calculated for $C_{10}H_9O_3N_3$: N, 19.18. Found: N, 19.33.

6-Nitro-2-methyl-3-ethyl-4-quinazolone, $CH_3.C : N.C_6H_3(NO_2).CO.N.C_2H_5$. —Five grams of the methylethylquinazolone were added to a mixture of 15 cc. concentrated sulfuric and 20 cc. fuming (sp. gr. 1.52) nitric acids, and the nitric acid boiled off. The cold acid solution was poured upon cracked ice, and the nitro derivative separated in short, fine needles which crumbled to a powder when thoroughly washed with water and dried. Yield, 80%. The compound showed the same melting point 166° (cor.) as recorded for this substance by Bogert and Cook,[1] who prepared it from the corresponding nitroanthranilic acid.

Dinitro-2-methyl-3-phenyl-4-quinazolone. — The methylphenylquinazolone was nitrated by a mixture of one part concentrated sulfuric to two parts fuming (sp. gr. 1.52) nitric acid, the solution concentrated, cooled, and poured upon cracked ice. The nitrated product separated in very fine, yellowish needles, not appreciably soluble in water, methyl or ethyl alcohols, ether, chloroform or benzene. From acetone, or from glacial acetic acid, it separates in microscopic crystals of faint yellowish cast, melting at 267° (uncor.). Yield, 65%.

Calculated for $C_{15}H_{10}O_5N_4$: N, 17.17. Found: N, 17.21.

The compound is evidently a dinitro derivative, and it was suspected that one nitro group had entered position 6, as usual, and that the other had probably attached itself to the 3-phenyl group, most likely in the para position, as is the case in nitrating 2-styryl-4-quinazolone.[2] Nitration of 2-methyl-3-*p*-nitrophenyl-4-quinazolone, as recorded beyond, did not give the same substance, and this part of the investigation was not carried further on account of the withdrawal of the junior author to take up other work. In our opinion, the compound is most probably the 6-nitro-2-methyl-3-*o*-nitrophenyl-4-quinazolone, since 2-methyl-3-*p*-tolyl-4-quinazolone also yields a dinitro derivative.

Nitro-2-methyl-3-p-nitrophenyl-4-quinazolone. — The nitration was carried out in a manner similar to that used in the previous cases, and showed that only one more nitro group could be introduced under these conditions. The position probably taken by the entering nitro group is at 6, as already explained. The product crystallized from glacial acetic acid in clusters of small, golden yellow scales, melting with decomposition at 264° (uncor.), and insoluble in water or alcohol.

Calculated for $C_{15}H_{10}O_5N_4$: N, 17.17. Found: N, 17.34.

A mixture of this with the foregoing dinitro body showed a melting point of 225° (uncor.).

Dinitro-2-methyl-3-p-tolyl-4-quinazolone. — The nitration of 2-methyl-3-*p*-tolyl-4-quinazolone in the same way also resulted in the production

[1] *Loc. cit.*

[2] Bogert and Beal, THIS JOURNAL, 34, 516 (1912).

of a dinitro derivative, insoluble in water or alcohol, but dissolving in glacial acetic acid. On diluting the latter solution, it separated in minute, pale yellow crystals, shriveling at 262° and melting with decomposition at 275° (uncor.). Yield, 1.2 g. quinazolone. We think it likely that one of the nitro groups in this compound is at position 6, and the other one in the *p*-tolyl nucleus.

Calculated for $C_{16}H_{12}O_5N_4$: N, 16.47. Found: N, 16.75.

IV. Reduction of the Nitro to the Corresponding Amino 4-Quinazolones.

Amino-4-quinazolone, $HC : N.C_6H_3(NH_2).CO.NH$. — The nitro compound was reduced with stannous chloride and hydrochloric acid, and the tin removed by hydrogen sulfide. After the elimination of the tin, the solution was made alkalin with potassium hydroxide, filtered, and the filtrate neutralized exactly. Feathery masses of short, fine needles separated. Recrystallized from water, these needles melted at 318° (cor.). Yield, about 20%. The substance is soluble in dilute acids or in alkalies.

Calculated for $C_8H_7ON_3$: N, 26.08. Found: N, 25.95.

Acetamino-4-quinazolone, from the aminoquinazolone and acetic anhydride, crystallizes from water in colorless, short, silky needles, melting at 335° (cor.). Yield, 90%.

Calculated for $C_{10}H_9O_2N_3$: N, 20.69. Found: N, 20.57.

6-Amino-2-methyl-4-quinazolone. — The nitroquinazolone was reduced with stannous chloride (or tin) and hydrochloric acid, and the reduction product separated as described for the amino-4-quinazolone. The yield was fair and the product, after recrystallization from water, melted at 314–5° (cor.), with preliminary softening at about 304°. It forms long, colorless, silky needles, soluble in dilute acids or alkalies. This product was found to be identical with the 6-amino-2-methyl-4-quinazolone prepared by Bogert, Amend and Chambers[1] from 2,5-diacetaminobenzoic acid. Both products showed the same melting point, and when the two were intimately mixed the melting point of the mixture was the same.

Dehoff[2] tried the above reduction of the nitroquinazolone but, apparently through lack of sufficient initial material, failed to get the amino compound.

Calculated for $C_9H_9ON_3$: N, 24.00. Found: N, 24.12.

6-Acetamino-2-methyl-4-quinazolone was obtained from the aminoquinazolone by the action of acetic anhydride and purified by crystallization from water. It forms fine, colorless needles which, when heated, turn brownish at about 335° and melt at 351° (cor.). Bogert, Amend

[1] THIS JOURNAL, 32, 1311 (1910).

[2] *Loc. cit.*

and Chambers prepared the same substance from 5-acetaminoacetanthranil and ammonia, and found its melting point to be 350° (cor.). A mixture of the two products showed a melting point of 349° (cor.), and in either respect they were found to be identical. When the 7-acetamino isomer (m. p. 344°, cor.) was mixed with this product, the melting point of the mixture dropped to 311° (cor.).

Amino-3-methyl-4-quinazolone, $HC:N.C_6H_3(NH_2).CO.NCH_3$.—The corresponding nitro compound was reduced with stannous chloride and hydrochloric acid, warming to complete the reaction. On cooling, colorless crystals separated. These were dissolved by adding three volumes of hot water, and the tin precipitated by hydrogen sulfide. The filtrate from the tin sulfide was boiled to remove hydrogen sulfide, then made alkalin, filtered hot, and on cooling the amine separated from the filtrate in small, colorless needles. Recrystallized from water, the substance melts at 209° (uncor.). Yield, 20%.

Calculated for $C_9H_9ON_3$: N, 24.00. Found: N, 23.96.

Acetamino-3-methyl-4-quinazolone, prepared from the above by the action of acetic anhydride, crystallizes from water in thin, colorless, silky needles, melting at 269° (uncor.).

Calculated for $C_{11}H_{11}O_2N_3$: N, 19.35. Found: N, 19.47.

6-Amino-2,3-dimethyl-4-quinazolone.—The corresponding nitroquinazolone was reduced with stannous chloride and hydrochloric acid, detinning with hydrogen sulfide, boiling out excess of the latter, filtering, making the filtrate alkalin and filtering hot. From this hot, alkalin filtrate, the amine separated on cooling and was recrystallized from water. It forms colorless, thin, silky needles, melting at 244° (uncor.). Yield, 10%.

Calculated for $C_{10}H_{11}ON_3$: N, 22.22. Found: N, 22.33.

6-Amino-2-methyl-3-ethyl-4-quinazolone was prepared in a similar manner from the nitro compound by reduction with stannous chloride and hydrochloric acid. It crystallizes from water in long, thin, colorless needles, melting at 185° (cor.). Yield, 20%.

Calculated for $C_{11}H_{13}ON_3$: N, 20.69. Found: N, 20.63.

V. Other Experiments with 2-Methyl-4-quinazolone.

The stability of this substance towards hot, concentrated hydrochloric acid under pressure was tested with the following results, using 5 cc. of the acid per gram of quinazolone:[1]

1. Six hours at 155°. No apparent change.

2. Six hours at 190°. Slight decomposition and some pressure in the tube. From 2 g. quinazolone, 1.8 g. of the hydrochloride were recovered.

3. Six hours at 216°. Partial decomposition, with considerable pressure in the tube. From 2 g. quinazolone, about 1.5 g. of the hydrochloride

[1] Compare Bogert and Seil, THIS JOURNAL, **28**, 890 (1906).

were recovered, and a small amount of what appeared to be aniline hydrochloride.

4. Six hours at 250°. Complete decomposition of the quinazolone into aniline, ammonia and carbon dioxide. Crystals of ammonium chloride separated in the tube.

2-Methyl-4-quinazolone and Benzoyl Chloride.—Ellinger and Riesser[1] found that, by the action of benzoyl chloride upon 4-hydroxyquinoline, 4-chlorquinoline could be obtained. It therefore seemed worth trying this reagent upon 2-methyl-4-hydroxyquinazoline (2-methyl-4-quinazolone), in the hope that here too the hydroxyl group might be replaced by chlorine, since all other methods so far used to get this chlorquinazoline have failed. Experiments directed to this end, however, proved unsuccessful. When a mixture of five grams of the quinazolone and 50 cc. benzoyl chloride were heated together, the quinazolone slowly dissolved, and in three hours a clear solution was obtained, but no chlorquinazoline could be recovered from the dark liquid.

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[FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY OF WASHINGTON UNIVERSITY, ST. LOUIS.]

STUDIES ON MALIC ACID. I. THE TRANSFORMATION OF MALIC ACID TO SUGAR BY THE TISSUES OF THE MAPLE (ACER SACCHARINUM).

BY W. R. BLOOR.

Received February 2, 1912.

Although malic acid is one of the most widely distributed plant acids, very little is known definitely of its chemical relations to the other organic plant substances, or of its function in the plant organism. Together with tartaric and citric acids, malic acid is generally regarded as a product of "intramolecular" respiration and, like them, is most closely related to glucose. In certain members of the Crassulaceae—thick-leaved desert plants which have adapted themselves to life in places where moisture and carbon dioxide are scarce—it has been demonstrated by Kraus[2] that there is an accumulation of malic acid at the expense of the sugar during the night, and a transformation of malic acid into sugar during the day. By this process of molecular rearrangement the plant is supplied with energy during the night while the precious carbon dioxide is preserved for use during the succeeding day. These same plants use malic acid also as a form of reserve material, the calcium malate deposited often amounting to half the dry weight of the leaf. The disappearance of malic acid accompanied by an increase of sugar is well known

[1] *Ber.*, 42, 3336 (1909).

[2] Kraus, *Abhandl. Naturforsch. Gesellsch. Halle*, 16, 393 (1886).