

testing, except where a special procedure is prescribed for the individual classes of thermometers in the foregoing regulations.

As a rule the errors observed are given for the thermometers in a vertical position and with the *whole* of the liquid column immersed in the bath.

If the use of the thermometer requires the liquid column to emerge from the bath whose temperature is to be measured, information must be given when the thermometer is sent in, as to how deep the thermometer must dip into the bath and what the temperature of the emergent column may be assumed to be.

18. *Charges for testing.*

19. Thermometers will be tested in the order of their receipt as shown by the post-mark; the preliminary tests will be made at once upon the receipt of the thermometer. The tests will be finished in from three to four weeks according to their nature and the amount of work on hand.

APPENDIX.

20. *Recommendations as to the packing and sending of thermometers.*

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 19.]

A NEW SYNTHESIS IN THE QUINAZOLINE GROUP.¹

(PRELIMINARY ANNOUNCEMENT.)

BY MARSTON TAYLOR BOGERT AND AUGUST HENRY GOTTHELF.

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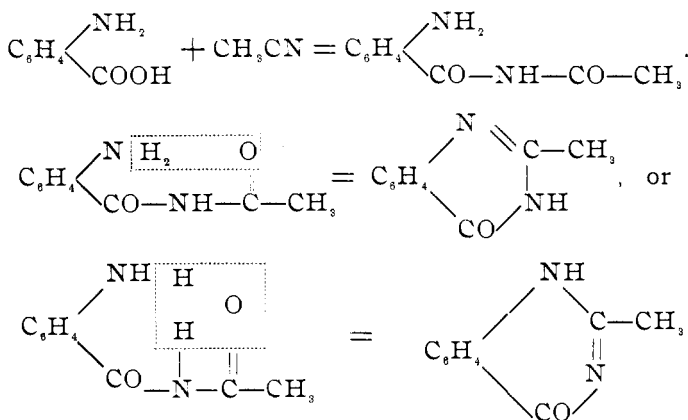
IN the course of some researches carried on in this laboratory by J. A. Mathews on "The Action of Nitriles upon Aromatic Acids,"² it was discovered that when anthranilic acid and acetonitrile were heated together in a sealed tube for five hours at 220°–230° C., instead of obtaining orthoamidobenzonitrile as expected, there resulted a crystalline product melting at 232°. This body was boiled with strong hydrochloric acid, and the solution on cooling deposited long needles which sublimed at about 280° without melting. Not enough of the substance, however, was secured for an analysis, and hence its nature could not be determined.

¹ Read before the New York Section, February 9, 1900.

² This Journal, 20, 654.

The writers have continued this investigation, and, by varying the conditions slightly, have readily obtained very fair yields of this substance and identified it as the 2-methyl-4-ketodihydroquinazoline first described by Weddige¹ and later obtained by Bischler and Burkart,² Bischler and Lang,³ and Niementowski⁴. The needles obtained by Mathews by the action of hydrochloric acid were, of course, only the HCl salt.

The reaction by which the quinazoline compound is produced from anthranilic acid and acetonitrile is easily explained when it is remembered that, under conditions of heat and pressure, a nitrile tends to combine with an organic acid to form a secondary amide, as shown first by Gautier,⁵ and later, in this laboratory, confirmed by the work of Colby and Dodge.⁶ The reaction, therefore, probably takes the following course :



As early as 1860, Griess and Leibius⁷ studied the action of cyanogen gas upon the amidobenzoic acids, and in 1869, Griess⁸ obtained condensation products by passing cyanogen gas into aqueous and alcoholic solutions of anthranilic acid. The condensation products, however, were due entirely to a preliminary

¹ *J. prakt. Chem.* (2), 31, 124.

² *Ber. d. chem. Ges.*, 26, 1350.

³ *Ibid.*, 28, 282.

⁴ *J. prakt. Chem.* (2), 51, 564; and *Ber. d. chem. Ges.*, 29, 1360.

⁵ *Ztschr. Chem.* (1869), 127.

⁶ *Am. Chem. J.*, 13, 1.

⁷ *Ann. Chem.* (Liebig), 113, 332.

⁸ *Ber. d. chem. Ges.*, 2, 415.

amidine union between the cyanogen and amido groups, which in our synthesis is very improbable, both on account of the less acid character of the nitriles employed and also because Berntsen has shown¹ that benzonitrile and aniline have no appreciable action upon each other even at 360° C. The products obtained would also be far different from those which we have separated.

The reaction of Niementowski,² by which he obtains quinazoline derivatives through the interaction of an amide upon anthranilic acid, appears to be a simultaneous condensation between the amido and carbonyl groups of the amide and the carboxyl and amido groups of the anthranilic acid, and is, possibly, in its internal mechanism, somewhat related to the nitrile synthesis under discussion. Niementowski found, however, that while the yield with formamide and acetamide was excellent, as the molecular weight of the amide increased it became less and less satisfactory, the higher temperature required producing more and more decomposition, and consequently more by-products, while with benzamide the condensation failed entirely and no quinazoline body could be obtained.

With our synthesis, on the other hand, using nitriles instead of amides, the reaction proceeds just as smoothly with aromatic nitriles as with aliphatic; the contents of the tubes are invariably crystalline and free from by-products (except a small amount of carbonaceous material), and by treating with boneblack and crystallizing twice from alcohol, the quinazoline body is obtained pure. We have thus prepared with the greatest ease the following derivatives of the 4-ketodihydroquinazoline, together with many of their salts:

2-Methyl.—Identical with that described by Weddige.³

2-Ethyl.—Already described by Bischler and Lang,⁴ and by Niementowski.⁵

2-Phenyl.—Isomeric with, but not the same as the phenyl derivative of Körner,⁶ the isomerism probably being due to a different position of the double bond in the miazine nucleus (at (1), instead of (2) ?).

¹ *Ann. Chem. (Liebig)*, 184, 349, foot-note.

² *J. prakt. Chem. (2)*, 51, 564.

³ *Ibid. (2)*, 31, 124.

⁴ *Ber. d. chem. Ges.*, 28, 284.

⁵ *J. prakt. Chem. (2)*, 51, 568.

⁶ *Ibid. (2)*, 36, 155.

2-Benzyl.—New.

2-Paratolyl.—New.

The description of these bodies and their derivatives, together with many others upon which we are now at work, will be presented later. So much work has been and is being done upon quinazolines that we have deemed it wise, before entering upon the very extensive field which this new synthesis opens up, to present this preliminary notice, that we may be left free to continue our work without fear of molestation.

We should like, therefore, to reserve for the Organic Laboratory of Columbia University, the study of the action of cyanogen compounds upon organic acids, as we shall endeavor to extend this research to bodies of the aliphatic series (in the hope of obtaining oxyprymidine compounds), as well as to other classes of compounds. We are also investigating the action of nitriles upon other ortho-substituted acids, etc., and upon closely related bodies.

When one considers the ease with which the nitriles can be obtained, especially in the aromatic series, and the fact that all the nitriles used so far, both aliphatic and aromatic, react with the same facility, it does not seem too much to say that this new process appears likely to prove the most widely applicable and most important synthesis for quinazoline compounds yet discovered.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, February 1, 1900.

A COMPARISON OF SOME FORMALDEHYDE TESTS.¹

By B. M. PILHASHY.

Received February 5, 1900.

HAVING had occasion to make some qualitative tests to show the presence of formaldehyde, I reviewed the recent chemistry for the detection of formaldehyde. In some instances the reaction given for formaldehyde proved to be true for other aldehydes also and apparently for distilled water. In some cases the delicacy of the reaction given for a particular reagent was not true for the stated dilution, while in others the reaction was clear and not to be doubted. The following summary of

¹ Read before the Cincinnati Section, November 13, 1899.