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 oxypyrimidine 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]

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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 15, 1899.

various reactions for the more common aldehydes may prove useful to others, who may have occasion to work in the same line.

(*a*) *Schiff's Reagent.*—Most aldehydes in dilute solutions give a violet coloration with this reagent. (Fuchsin decolorized by sulphurous acid.) This can also be obtained by mere exposure of the reagent to the air or by warming the suspected liquid with the reagent even in the absence of an aldehyde.[1]

(*b*) *Phenol and Sulphuric Acid.*—Most aldehydes give with very dilute phenol and sulphuric acid added to form a layer beneath, a scarlet ring changing to dark red on heating.[2]

(*c*) *Diazobenzenesulphonic Acid.*—Most aldehydes with this reagent in the presence of free alkali and sodium amalgam give an intense violet color at once or within twenty minutes. The colors are destroyed by exposure or by acid.[3]

(*d*) *Nessler's Solution.*—Acetaldehyde as well as formaldehyde gives a precipitate with Nessler's solution. They also give a precipitate with anilin.[4]

(*e*) *Dimethylanilin and Sulphuric Acid.*—Trillat gives the following reaction for formaldehyde alone. To a dilute solution a few drops of sulphuric acid and also of dimethylanilin are added. The mixture is heated for half an hour on a water-bath, made alkaline and further heated to drive off the excess of dimethylanilin which can be detected by its odor. The liquid is then filtered and the paper moistened with acetic acid. If formaldehyde is present, a blue coloration results when lead dioxide is then sprinkled on the paper.[5]

The following experiments tend to show that this reaction is due to dimethylanilin present.

Experiment 1.—If a piece of filter-paper be moistened with a very dilute solution of dimethylanilin in water it will give the blue color reaction with lead dioxide and acetic acid.

Experiment 2.—Twenty cc. distilled water, 2 drops of sulphuric acid, and 1 drop of dimethylanilin were mixed, forming

1 Allen's "Commercial Organic Analysis," Vol. I, 3rd edition, p. 217.

2 *Ibid.*

3 *Ibid.*

4 *Ibid.*

5 *Ibid.*, p. 220.

a very dilute acid solution. This was heated one-half hour, during which time 100 cc. distilled water were added at intervals to replace that evaporated. After heating a while a strip of filter-paper dipped into this solution gave a yellow color with lead dioxide and acetic acid. Another strip dipped into the solution and made alkaline with ammonium hydroxide or sodium carbonate solution gave a slight blue after ten minutes. At the end of the heating these reactions could not be again obtained pointing to a probable volatilization of the salt formed.

Experiment 3.—Instead of the distilled water in Experiment 2, 20 cc. formaldehyde solution (1 : 1000) were used. After heating for one-half hour a strip of filter-paper moistened with the solution gave the yellow color observed in Experiment 2, with the lead peroxide and acetic acid and the blue color with the same reagents after making alkaline. The outside of the dish was coated with a yellow salt which was washed into a dish, made alkaline and filtered. The filter-paper gave the before-mentioned blue reaction.

Experiment 4.—A few drops of dimethylanilin were dissolved in water with the aid of a few drops of sulphuric acid. A strip of paper moistened with it gave the yellow reaction with lead peroxide and acetic acid. The solution was neutralized and filtered. The filter-paper as well as a strip moistened with the solution gave the blue coloration as above.

Experiment 5.—Twenty cc. formaldehyde solution (1 : 1000), 2 drops of sulphuric acid, and 1 drop of dimethylanilin were heated for one-half hour, made alkaline with sodium hydroxide solution and then heated for one hour longer to drive off any free dimethylanilin in excess. There was no odor to the solution which was filtered. The filter-paper gave no blue coloration with lead peroxide and acetic acid.

SUMMARY.

From the foregoing experiments it seems that Trillat's test does not show the presence of formaldehyde, but of dimethylanilin or its salts when not completely volatilized.

(*f*) *Lebbin's Test.*[1]—This is said to be delicate enough to detect 1 part formaldehyde in 10,000,000 of water. In my experience 1 in 200,000 seems to be the limit.

(*g*) *Morphin hydrochloride*[2] with sulphuric acid is not to be considered sensitive enough for formaldehyde in a more than 1 : 1000 solution, a purple ring being obtained.

(*h*) *Phenylhydrazin hydrochloride*[3] seems to be the best reagent for formaldehyde. The solution of 1 gram of phenylhydrazin hydrochloride with 1.5 grams sodium acetate in 10 cc. water is used. To 1 cc. of the liquid 2 drops of the reagent and 2 drops of sulphuric acid are added producing a green coloration. In as dilute a solution as 1 : 10,000 or 1 : 100,000, 3 cc. of the liquid with 4 drops of the reagent and 4 drops of sulphuric acid heated for half a minute bring out the color. For 1 : 250,000, 3 cc. of the liquid with 5 drops of the reagent and 5 drops of sulphuric acid heated for about a minute, give a very light tinge of green after three minutes, a decided tint after ten minutes.

(*i*) Rimini[4] uses *phenylhydrazin hydrochloride with sodium nitroprusside and concentrated sodium hydroxide*, a blue coloration resulting. One part in 1,000 and 1 in 10,000 give an intense blue when 1 cc. of the solution is mixed with 2 drops each of phenylhydrazin hydrochloride solution and of sodium nitroprusside solution, 1 cc. of caustic soda solution being then added. One in 100,000 gives a deep blue, and one in 1,000,000 gives a light blue. These blues change quickly to green, yellow, light brown, and red. A peculiarity is the rise of the red color to the top leaving a yellow layer below. Both layers are clear solutions. If the same amount of reagent as given above be added to dilutions greater than 1 in 1,000,000, about the same shade of blue is obtained for them,—hence the limit seems to be 1 in 1,000,000.

1 Allen's "Commercial Organic Analysis," Vol. I, 3rd edition, p. 220.
2 *J. Soc. Chem. Ind.*, Abst., p. 955 (1898).
3 *Ibid.*, p. 954.
4 *Ibid.*, p. 697.