NEW REAGENTS FOR THE COLORIMETRIC DETERMINATION OF NITRITE

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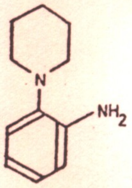
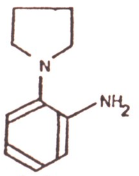
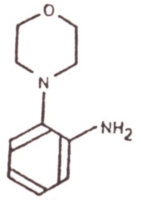
During an investigation of the properties of certain nitrogen heterocycles of types (I, II, III) which were needed for another research, it was noted that each of these compounds on treatment with nitrous acid gives an intensely coloured, relatively stable solution of its diazonium salt.


(I)


(II)


(III)

The water-soluble hydrochloride of *N*-(2-aminophenyl)-piperidine (I) for instance, develops in the presence of nitrite ions an intense orange colour which shows its maximum absorption at a wavelength of $\gamma = 445$ mμ. Beer's Law is found to be obeyed for nitrite concentrations between 0·1 μg. NO_2^-/ml. and 20μg. NO_2^-/ml. The full intensity of colour is not developed instantly and the time taken for this is governed by temperature as indicated in the Table.

Table

Time (min.) (After mixing solutions)	*Total Absorption (%) at 445 mμ* 18°	30°
1	23	—
5	53	—
10	72	84
20	88	95
25	92·5	100
35	98·5	99
40	99	98·5
60	100	94

When kept in the dark at *ca.* 18° the diazonium solution remains stable for up to 24 hours and the loss in colour intensity even then is less than 1%. It was found practicable to carry out absorption measurements at 18–20° after the reaction mixture had been allowed to stand in the dark for 40 minutes. The colour development is not interfered with by a hundredfold excess of the reagent or by the presence of various ions including nitrate up to a concentration of 200 μg./ml.

Interference is, however, caused by oxidising agents, e.g. Ce^{4+}, Fe^{3+}, and $Cr_2O_7^{2-}$ when present in concentrations greater than 10μg./ml. and VO_4^{2+}, MnO_4^{1-}, and H_2O_2 at concentrations greater than 50 μg./ml. Addition of fluoride ion before nitrite addition prevents interference by Fe^{3+} (fluoride itself does not interfere).

The base *N*-(2-aminophenyl)pyrrolidine (II) was of limited use since exposure to light quickly converts it into a brown liquid.

N-(2-Aminophenyl)morpholine (III) gives a soluble, intensely coloured diazonium salt with a maximum absorption at $\lambda = 435$ mμ. The rate of colour development is fast and no change in the colour intensity was observed after 30 seconds from mixing the reagents. The molar extinction coefficients of the diazonium compounds derived from (I) and (III) are approximately equal. The bases[1,2] (I, II, III) were made by condensation of 1-chloro-2-nitrobenzene with the appropriate heterocycle followed by reduction (iron and ammonium chloride[3] or Raney Nickel and hydrogen) of the resulting nitro-compound. The pyrrolidine compound is a colourless liquid, b.p. 91–94°/0·1 mm.

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