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An investigation of why 1-aminophenazine fails to form a diazonium salt which will couple with  $\beta$ -naphthol revealed that the phenazine-1-diazonium cation reacts rapidly with water to give 1-diazo-2-(1*H*)phenazinone (**1**), whose coupling ability has been demonstrated to be very weak. A similar reaction occurred with 2-aminophenazine.

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Ramage and Landquist (1) have reported that the diazotization of 1-aminophenazine failed, since no azo coupling products were formed on addition of phenols. We have reported (2) that the diazotization of 1-amino-2-ethoxyphenazine yielded the stable 1-diazo-2-(1*H*)phenazinone (**1**), via a rapid displacement of the ethoxy group of the highly activated diazonium salt by water. The unreactivity of this diazo compound was demonstrated by its failure to react with  $\beta$ -naphthol to form an azo dye. With the more powerful nucleophile, phloroglucinol, the coupling reaction of **1** did occur, giving a red azo compound.

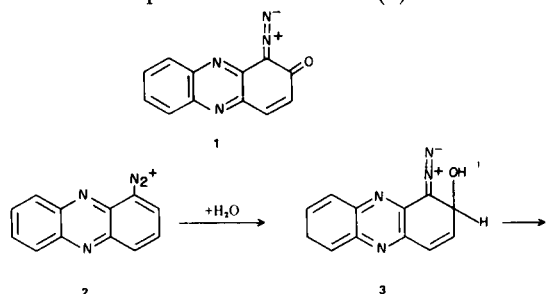
When the diazotization of 1-aminophenazine was repeated, it was found that coupling with  $\beta$ -naphthol did not occur, whereas coupling with phloroglucinol did occur. An answer to the question of why coupling of the diazonium salt from 1-aminophenazine should be observed only with very reactive phenols was sought. Since the phenazine system is known to be electrophilic, the diazo group should couple more readily in the 1-diazonium salt.

When the diazotization reaction of 1-aminophenazine was diluted with water, the precipitation of a yellow material occurred, and this was shown to be 1-diazo-2-(1*H*)phenazinone (**1**), the same product which resulted from the diazotization of 1-amino-2-ethoxyphenazine (2). This conversion to the weakly coupling 1-diazo-2-(1*H*)phenazinone, takes place rapidly and completely, so that none of the phenazine-1-diazonium salt (**2**) was actually present when the  $\beta$ -naphthol tests were carried out.

We postulate the phenazine-1-diazonium salt (**2**) was rapidly attacked by water at the highly activated *ortho* position, to give the intermediate **3** (1-diazo-1,2-dihydro-2-hydroxyphenazine). Oxidation of **3** or the dihydrophenazinone tautomer of **3** by molecular oxygen or nitrous acid would be expected.

To test the generality of the diazotization reaction of aminophenazines, 2-aminophenazine was also treated with nitrous acid followed by water dilution. Chromatography of the products gave a small yield (16%) of a diazoketone mixture and phenazine (30%). The ir spectrum of the diazoketones showed two intense diazo absorptions (2125 and 2147  $\text{cm}^{-1}$ ) and possible two strong carbonyl absorptions (1625 and 1572  $\text{cm}^{-1}$ ) suggestive of the presence of 2-diazo-1-(2*H*)phenazinone and 3-diazo-2-

(3*H*)phenazinone. The phenazine may have resulted from the reduction of the phenazine-2-diazonium salt during oxidation of an intermediate 2-diazo-1,2-dihydro-1-hydroxyphenazine or 2,3-isomer to the phenazinone product. Early workers isolated only phenazine from the diazotization of 2-aminophenazine in ethanol (3).



## EXPERIMENTAL

1-Aminophenazine (1.0 g.), prepared by the method of Otomasu (4), was dissolved in 5.0 ml. of concentrated hydrochloric acid. This solution was cooled to 0° and a solution of 0.35 g. of sodium nitrite in 1 ml. of water was added slowly. After two minutes the reaction was diluted with 20 ml. of water. Filtration of the yellow precipitate yielded 1.04 g. of 1-diazo-2-(1*H*)phenazinone, identical to that prepared by diazotization of 1-amino-2-ethoxyphenazine (2). The identity was established by superimposable ir spectra, melting points and thin layer  $R_f$  values.

The 1-diazo-2-(1*H*)phenazinone from either source yielded an azo coupling product with phloroglucinol in basic ethanol,  $\lambda_{\text{max}}$  500 nm ( $\epsilon = 1.0 \times 10^4$ ).

2-Aminophenazine (5) (1 g.) was diazotized in the above manner and the crude precipitate was dissolved in benzene and chromatographed on alumina rapidly with hexane-benzene. The first fractions yielded phenazine (0.33 g., 30%) and later fractions gave the diazoketone mixture (0.18 g., 16%). Separation of the diazoketones was unsuccessful. The ms of the mixture exhibited peaks at similar *m/e* to those of 1-diazo-2-(1*H*)phenazinone (2); ms: 222, 194, 166, 139 *m/e*; ir (potassium bromide): 3050, 3025, 2920, 2125, 2147, 1625, 1572, 1525, 1347, 1274, 1222, 1085, 979, 892, 814, 758, 738.

## REFERENCES AND NOTES

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