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Abstract:

Enediamines was prepared by simple reaction of arylazomalononitrile with piperidine or morpholines in high yield. Reaction of the obtained enediamines with acid and hydrazines was studied. Structure of the novel eneditimes was established by x-ray data as well as, spectroscopic and analytical data.

Introduction:

Recently the chemistry of push-pull enamines is the subject of many reports owing to their successful utility as a starting materials for the synthesis of various substituted heterocycles. In spite of this importance, very little attention was paid to the synthesis, rather than the utility of enediamines. The known method for enediamines of the type 3 was obtained by ring opening of 6-substituted amino-4-chloro-5-nitropyrimidines (1) under acid hydrolysis which was converted to the a,a-diamino-β-cyano-β-nitroethylenes (3) which mainly contaminated with by-products and obtained in poor yields after 6 successive steps (cf. Scheme 1). Also, only one known report for the preparation of azaenediamines 4a,b described, for surprising, as colourless compounds.

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**Key Words:** Arylazonitriles / piperidine / morpholine / azaenediamines

\[
\begin{align*}
1 & \quad \text{4 Steps} \\
& \quad \text{in aq. HCl} \\
2 & \quad \text{eq. } \text{NH}_2 \\
3 & \quad 2a, R^1 = R^2 = \text{Me} \\
& \quad b, R^1 = \text{H}, R^2 = \text{Ph} \\
4 & \quad \text{4a, } X = \text{O} \\
& \quad b, X = \text{CH}_2
\end{align*}
\]

Scheme 1

**Results and Discussion:**

In the present work, \(\alpha,\alpha\)-diamino-\(\beta\)-cyano-\(\beta\)arylazoethylene (6) was obtained in pure state and in high yields by heating the arylazomalononitriles 5 with piperidine or morpholine in a molar ratio (1:1.2) in ethanol for few minutes. Structure of the obtained enediamines was established by elemental analysis, IR, \(^1\)H-NMR, C\(^{12}\)-NMR, and X-Ray analysis of 6c which confirm the E,E-configuration\(^8\) of the obtained enediamines (cf. experimental).
Table 1: Selected Bond angles of 6c

<table>
<thead>
<tr>
<th>INTRAMOLECULAR BOND ANGLES</th>
<th>Bond length limits use covalent radii +0.20Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(3)-N(2)-C(13)</td>
<td>118.7(3)</td>
</tr>
<tr>
<td>N(1)-C(8)-N(5)</td>
<td>119.2(4)</td>
</tr>
<tr>
<td>N(5)-C(8)-C(13)</td>
<td>117.7(4)</td>
</tr>
<tr>
<td>C(8)-C(13)-C(11)</td>
<td>121.3(4)</td>
</tr>
<tr>
<td>N(2)-N(3)-C(17)</td>
<td>111.0(3)</td>
</tr>
<tr>
<td>N(1)-C(8)-C(13)</td>
<td>123.1(4)</td>
</tr>
<tr>
<td>N(2)-C(13)-C(11)</td>
<td>122.2(4)</td>
</tr>
</tbody>
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Table 2: Selected Bond Lengths of 6c

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in contrast to the reported formation of colourless arylazoenediamines derivatives\(^7\), deepening and lightening of colour was observed in conversion of 5 to 6. This is logic due to the presence of extra bathochromic group (NH\(_2\) and tertiary amines) together with the increasing of conjugation pattern.

The obtained enediamines was converted to the starting arylazo analogues by the action of acid (acetic acid glacial). Also, reaction of 6a-d with hydrazines gave easily the corresponding known 3,5-diaminopyrazoles\(^{9,10}\) 9a-d in high yields.

The most probable mechanism for formation of 9 may be summarized in Scheme 2. Compounds 9 was found identical with those obtained from reaction of 5 with hydrazines, via elimination of the more bulky substituette.
Scheme 2
Experimental:

Melting points were measured on Barnstead Electro-chemical melting point apparatus and were not corrected. Elemental analysis for C, H and N were performed using a Thermo Finnigan Flash EA1112 instrument. -IR spectra were recorded (KBr) with Pye nicam SP-1100 spectrophotometer. – ^1H-NMR and ^13C-NMR spectra were measured in DMSO on a Brucker 500 spectrophotometer and chemical shifts were expressed in ppm downfield from tetramethylsilane. Mass spectra were recorded on a Finnigan-MAT 8430 spectrometer at an ionization potential 70 ev.

Preparation of arylozenediamines 6a-d

**general Procedure**- To a solution of 5 (0.01 mol) in absolute ethanol (30 ml) was added piperidine or morpholine (0.012 mol). The reaction mixture was refluxed for 2 hours. The precipitate formed on cooling was collected by filtration and crystallized from chloroform-ethanol mixture.

(EE)-3-amino-2-(phenyldiazinyl)-3-(piperidin-1-yl)acyronitrile (6a): Yield 97%, m.p. 168 °C dark orange crystals. –IR: v =3410-3272 cm⁻¹(NH2), 2183 (CN),^1H-NMR: δ =1.65(m, 6H, 3CH2 piperidine), 3.29-3.55(m, 4H, 2CH2 piperidine), 7.09-7.53 (m, 7H, ArH+NH2).

(EE)-3-amino-2-(phenyldiazinyl)-3-(morpholin-1-yl)acyronitrile (6a): Yield 91%, m.p. 183 °C, bright brown crystals, -IR: v 3440-3274 cm⁻¹ (NH2), 2190 (CN).^1H-NMR: δ=3.59-3.69, 3.71-3.72 (2t, 8H, j =4.73 Hz, CH2 morph.), 7.1-7.6 (m, 7H, 5ArH+NH2).

3,5-Diamino-4-phenylazo-1H-pyrazole (9a). Yield 85%, m.p. 263°C (lit.2 m.p.255°C).

3,5-Diamino-4-phenylazo-1-phenylpyrazole (9b). Yield 81%, m.p. 178°C (lit.9 m.p.174°C).

3,5-Diamino-4-(4-methoxyphenylazo)-1H-pyrazole (9c). Yield 78%, m.p. 261°C (lit.10 m.p.259°C).

3,5-Diamino-4-(4-methoxyphenylazo)-1-phenylpyrazole (9d). Yield 81%, m.p. 149°C (lit.10 m.p.157°C).
REFERENCES:

8. Crystallographic data for the structural analysis for compound 6c have been deposited at the Cambridge Crystallographic data centre, CCDC No. 791928.