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> SHORT COMMUNICATIONS

## Formation of 1-Aminophenazine from 3,4-Dihydrophenazin-1(2*H*)-one Oxime in the System Acetylene–KOH–DMSO

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**Abstract**—The reaction of 3,4-dihydrophenazin-1(2*H*)-one oxime with acetylene in the superbasic system KOH–DMSO afforded 1-aminophenazine in 32% yield instead of the expected pyrrolophenazine. The same product was also obtained under analogous conditions in the absence of acetylene.

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Cyclohexanone oxime is readily converted to 4,5,6,7-tetrahydroindole in the reaction with acetylene in the system KOH–DMSO [1–5]. More complex compounds containing a six-membered cyclic ket-oxime fragment, e.g., oximes derived from substituted cyclohexanones [4–6], tetralones [4, 5, 7], piperidinones [4, 5, 8, 9], cyclohexanediones [4, 5, 10, 11], and steroidal ketones [4, 5, 12, 13], behave in a similar way. In all cases without exception the oxime fragment is transformed to pyrrole ring (Trofimov reaction) [14–16].

It might be expected that the reaction of 3,4-dihydrophenazin-1(2H)-one oxime (1) with acetylene under analogous conditions would lead to the formation of pyrrole-fused phenazine **2**. However, instead of pyrrolophenazine **2**, the product was 1-aminophenazine **3** (yield 32%; Scheme 1), whereas even traces of compound **2** were not detected in the reaction mixture. We also found that amine **3** is formed in the system KOH–DMSO in the absence of acetylene, other conditions being equal, though the reaction rate was lower (according to the <sup>1</sup>H NMR data, the conversion of **1** was ~50%).

As we showed previously [4, 5, 17], cascade assembly of pyrrole ring from oximes and acetylene involves intermediate formation of iminoaldehyde as



150



3,3-sigmatropic rearrangement product of the corresponding *O*-vinyloxime. In our case, *O*-vinyloxime is likely to be converted to iminoaldehyde **5**. Elimination of acetaldehyde molecule from the latter gives imine **6** which tautomerizes to amine **3** (Scheme 2). The driving force of the elimination of acetaldehyde from iminoaldehyde **5** may be formation of more stable aromatic system **3**. This should also be favored by thermodynamic stability of acetaldehyde as a good leaving group.

Presumably, the observed redox aromatization of oxime 1 in the absence of acetylene begins with proton abstraction from the  $\alpha$ -position with respect to the oxime group in 1 by the action of KOH–DMSO superbasic system (Scheme 3). Dianion A thus formed exists in equilibrium with singly charged *N*-hydroxy tautomer and is converted to hydroxylamine **B**. Deprotonation of the latter at the 3-position gives dianion C which loses hydroxide ion to form imine 6, and the subsequent aromatization of 6 yields amine 3.

1-Aminophenazine (3) was synthesized previously from oxime 1 in two steps, via reaction with acetic anhydride, followed by hydrolysis of the resulting amide [18].

The discovered transformations supplement the chemistry of oximes and acetylene and extend the scope of application of superbasic systems as reagents and catalysts in organic synthesis; their efficiency and versatility are continuously confirmed by new examples [19–24].

**Phenazin-1-amine (3).** *a*. Acetylene was passed over a period of 2 h through a mixture of 0.425 g (2.0 mmol) of oxime **1** and 0.128 g (2.0 mmol) of potassium hydroxide hemihydrate in 5 mL DMSO under stirring at 93–96°C. The mixture was cooled and diluted with brine, 0.112 g (2.1 mmol) of ammonium chloride was added, and the mixture was extracted

with diethyl ether ( $8 \times 7$  mL). The combined extracts were washed with water  $(3 \times 5 \text{ mL})$  and dried over anhydrous potassium carbonate, and the solvent was removed to leave 0.078 g (20%) of a dark red powder with mp 176–177°C (from MeOH); published data [18]: mp 179–181°C. The aqueous phase was additionally treated with methylene chloride ( $5 \times 7$  mL), the combined extracts were washed with water  $(3 \times 5 \text{ mL})$ and dried over K<sub>2</sub>CO<sub>3</sub>, and the solvent was removed to obtain an additional amount of amine 3, 0.047 g (12%). Overall yield 32%. IR spectrum (KBr), v, cm<sup>-1</sup>: 3467, 3333, 3057, 2921, 2854, 1620, 1517, 1465, 1391, 1357, 1136, 962, 763. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 5.24 br.s (2H, NH<sub>2</sub>), 6.91 d (1H, 2-H, J = 7.2 Hz), 7.55 m (1H, 4-H), 7.62 m (1H, 3-H), 7.77 m (2H, 7-H, 8-H), 8.18 m (2H, 6-H, 9-H).  $^{13}$ C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{C}$ , ppm: 107.7, 117.3, 129.4, 129.5, 129.7, 130.4, 132.1, 135.3, 141.3, 143.8, 144.1, 144.2. The spectral data coincided with those given in [25]. Mass spectrum: m/z 195 ( $I_{rel}$  100%)  $[M]^{+}$ . Found, %: C 74.02; H 4.57; N 21.39. C<sub>12</sub>H<sub>9</sub>N<sub>3</sub>. Calculated, %: C 73.83; H 4.65; N 21.52.

b. A mixture of 0.042 g (0.2 mmol) of oxime 1 and 0.013 g (0.2 mmol) of KOH $\cdot$ 0.5H<sub>2</sub>O in 0.5 mL of DMSO was stirred for 2 h at 92–94°C. The mixture was cooled and diluted with brine (4–4.5 mL), 0.011 g (0.2 mmol) of ammonium chloride was added, and the mixture was extracted with diethyl ether (7×2 mL). The combined extracts were washed with water (2×3 mL) and dried over potassium carbonate, and the solvent was removed. The residue was 0.009 g of a dark red powder which was a mixture of initial oxime 1 and amine 3 at a ratio of ~1:1 (<sup>1</sup>H NMR, CDCl<sub>3</sub>).

The IR spectrum was recorded on a Varian 3100 FT-IR spectrometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13 and 100.6 MHz, respectively, using hexa-

methyldisiloxane as internal standard ( $\delta$  0.05 ppm). The mass spectra (electron impact, 70 eV) were obtained on a Shimadzu GCMSQP5050A instrument.

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