

SHORT
COMMUNICATIONS

Iodine-Catalyzed Ketazines Cyclization into 2-Pyrazolines

B. F. Kukharev, V. K. Stankevich, and V. A. Kukhareva

Faworsky Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
Irkutsk, 664033 Russia
e-mail: irk_inst_chem@irioch.irk.ru

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Ketazines are known to undergo cyclization into 2-pyrazolines under the action of protonic acids. Dicarboxylic acids are considered to be the most active catalysts for ketazines cyclization [1, 2]. The reaction is performed in the presence of an equimolar amount of the acid and often requires additional heating. The pyrazoline forms not in the form of a base but as a pyrazolinium salt of the corresponding acid, therefore the reaction mixture should be treated with strong bases. Yield of pyrazolines reaches from 50 to 81% [2].

We found that by adding to acetone azine (**Ia**) 0.5 wt% of crystalline iodine a strong self-heating was observed (to 125–130°C), and after maintaining the reaction mixture at this temperature for 1 h the GLC analysis showed a complete conversion of the azine into

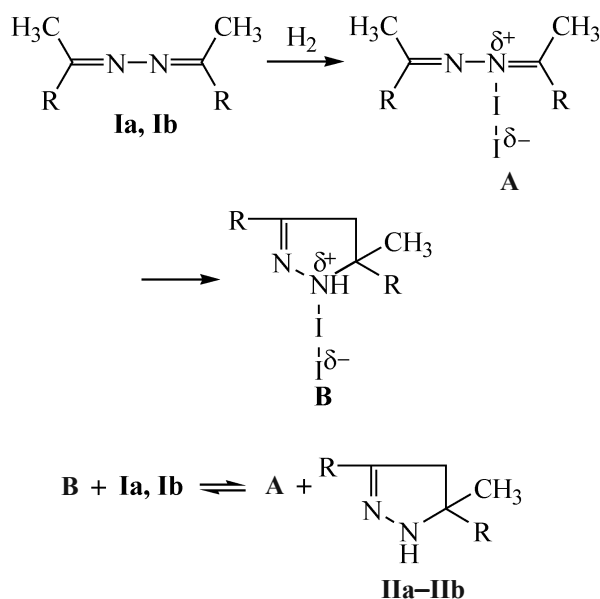
3,5,5-trimethylpyrazoline (**IIa**). The pyrazoline was isolated by distillation in 94% yield. Compare the acetone azine cyclization with anhydrous oxalic acid at azine to acid molar ratio 1:1.1: After 4-hour heating on a water bath the pyrazoline forms in 78% yield [2].

It is presumable that initially forms a complex of azine with iodine **A** where (same as in the catalysis with acids) because of a positive charge arising on the nitrogen the intramolecular condensation of crotonic type is facilitated and leads to a complex pyrazoline–iodine **B**, which reacting with azine **Ia** provides the base pyrazoline **IIa** and the azine complex with iodine **A**.

Evidently since the iodine unlike the proton is a mild acid [3] the equilibrium (2) is more shifted to the right than the similar equilibrium involving the protonated azine and pyrazoline. This event provides for the reaction proceeding in the presence of the catalytical quantity of iodine.

3,5,5-trimethyl-2-pyrazoline (IIa). To 11.22 g (0.1 mol) of acetone azine (**Ia**) was added at room temperature while stirring 0.05 g (0.2 mmol) of I₂. The reaction mixture self-heated to 125–130°C and was kept at 130°C for 1 h. After a vacuum distillation the yield of the product was 10.55 g (94%), bp 57–59°C (20 mm Hg), d_4^{20} 0.9011, n_D^{20} 1.4571 {bp 52.5°C (15 mm Hg), d_4^{20} 0.9025, n_D^{20} 1.4573 [2]}. ¹H NMR spectrum, δ , ppm: 1.24 s [6H, C(CH₃)₂], 1.92 s (3H, N=CCH₃), 2.40 s (2H, CH₂), 4.01 br.s (NH). Found, %: C 64.30; H 10.69; N 25.01. C₆H₁₂N₂. Calculated, %: C 64.24; H 10.78; N 24.97.

5-Methyl-3,5-diethyl-2-pyrazoline (IIb). To 14.2 g (0.1 mol) of methyl ethyl ketone azine (**Ib**) was added at room temperature while stirring 0.05 g (0.2 mmol) of I₂. The reaction mixture self-heated to 50–60°C, then it was heated for 1 h at 140°C. After a vacuum distillation the



yield of the product IIb was 12.78 g (90%), bp 107–109°C (20 mm Hg), d_4^{20} 0.9984, n_D^{20} 1.4872 {bp 148–152°C (107 mm Hg), d_4^{20} 0.9963, n_D^{20} 1.4860 [2]}. ^1H NMR spectrum, δ , ppm (J , Hz): 0.89 t (3H, $\text{CH}_3\text{CH}_2\text{CN}$, 3J 7.4), 1.10 t (3H, $\text{CH}_3\text{CH}_2\text{C}=\text{N}$, 3J 7.5), 1.17 s (3H, CH_3CN), 1.54 q (2H, $\text{CH}_3\text{CH}_2\text{CN}$, 3J 7.4), 2.26 q (2H, $\text{CH}_3\text{CH}_2\text{C}=\text{N}$, 3J 7.5), 2.32 d (1H, $\text{N}=\text{CCH}_\text{A}\text{H}_\text{B}$, 2J 16.4), 2.45 d (1H, $\text{N}=\text{CCH}_\text{A}\text{H}_\text{B}$, 2J 16.7), 4.27 br.s (NH). Found, %: C 68.43; H 11.48; N 20.08. $\text{C}_8\text{H}_{16}\text{N}_2$. Calculated, %: C 68.52; H 11.50; N 19.98.

REFERENCES

1. Kost, A.N. and Ershov, V.V., *Usp. Khim.*, 1958, vol. 27, p. 431; Langenbeck, W., *Die Organischen Katalysatoren und Ihre Beziehungen zu den Fermenten*, Berlin: Springer-Verlag, 1949.
2. Kost, A.N. and Grandberg, I.I., *Zh. Obshch. Khim.*, 1957, vol. 27, p. 1717.
3. *Chemical Reactivity and Reaction Paths*, Klopman, G., Ed., New York: Wiley, 1974.