FORMATION OF 1,2,4-TRIAZOLES BY THE ACTION OF ANGELI'S SALT ON SECONDARY AMINES AND ALKYLHYDRAZONES

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Two years ago we reported [1] the presence of one of the isomeric triazoles $C_6H_{11}N_3$ – apparently 3,5-dimethyl-1-ethyl-1,2,4-triazole – in the products of the reaction of Angeli's salt with diethylamine.

A genuine sample of I, obtained by the Einhorn–Brunner reaction [2] from diacetylamine and ethylhydrazine under the conditions used for the synthesis of the 1,3,5-trimethyl derivative [3], had bp 91-91.5° (19 mm), n_D^{20} 1.4649, and d_4^{20} 0.9834. The PMR spectrum was identical to the spectrum of preparation I obtained from Angeli's salt, and their mass spectra (obtained with an LKB-2091 spectrometer at 70 eV) coincided completely – m/e (relative intensity, %): 69 (100), 42 (85), 97 (26), 27 (26), and 125 (24, M^+). The IR spectra differed only with respect to the absence of weak bands at 1630 and 1565 cm^{-1}, whereas the "fingerprint" regions coincided. The certain discrepancy between the constants and spectra is explained by the extremely high hygroscopicity of triazole I and the presence of a difficult-to-separate impurity in the preparation obtained from diethylamine and Angeli's salt. In fact, when a saturated alcohol solution of picric acid is added to the latter, a picrate with mp 158.5° forms initially, followed by a picrate with the composition $C_6H_{11}N_3 \cdot C_6H_3N_3O_7$ (the results of elementary analysis are in conformity with the calculated values) and mp 125.5-126°; the latter picrate was identical to the picrate of authentic I with respect to its melting point [3] and the absence of a depression of the melting point of a mixture of the two substances.

3,5-Diethyl-1-n-propyl-1,2,4-triazole [PMR spectrum in $CHCl_3$: triplets at δ 0.92, 1.31, and 1.36 ppm (J = 7.3 Hz), sextet at 1.86 ppm (J = 7.3 Hz), quartets at 2.67 and 2.70 ppm (J = 7.3 Hz), and triplet at 4.00 ppm (J = 7.3 Hz) with an intensity ratio of 3:3:3:2:2:2:2] was detected in the products formed under similar conditions [1] from di-n-propylamine and $Na_2N_2O_3$. Mass spectrum, m/e: 83 (100), 125 (88), 124 (75), 167 (55, M^+), 138 (39). The picrate had mp 124.2°.

Thus we are dealing with a new instance of the formation of a symmetrical triazole ring that cannot be listed with known reactions for the synthesis of triazoles [2]. The triazoles are evidently secondary products of the reaction of Angeli's salt with dialkylamines and are formed from the alkylhydrazones:

$$RCH_2NHR' + HN_2O_3^- \longrightarrow NO_2^- + H_2O + RCH{=}NNHR' \quad (1)$$

$$2\,RCH{=}NNHR' + HN_2O_3 \longrightarrow \text{(triazole)} + NO_2^- + 2\,H_2O + R'NHNH_2 \quad (2)$$

The increase in the yields of the triazoles that we observed when alkylhydrazones were added to the mixture of secondary amines and Angeli's salt and the direct realization of the reaction of Angeli's salt with alkylhydrazones (2) constitute evidence in favor of this assumption. A total of 0.80 g of an organic layer containing, according to the results of gas-liquid chromatography, 0.002 mole [40% yield with respect to scheme (2)] of triazole I was obtained from a mixture of 0.01 mole of acetaldehyde ethylhydrazone and 0.011 mole of trimethylamine hydrochloride in 5 ml of water with a solution of 0.011 mole of $Na_2N_2O_3$ in 3 ml of water after heating at 60° for 1.5 h and salting out with NaOH.

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The known methods for the synthesis of sym-triazoles are characterized by much lower yields. For example, in the condensation of carboxylic acid hydrazides with amides (the Pellizzari reaction [2]) the yields of the triazoles do not exceed 15-20%, so that reaction (2) may be of preparative interest.

LITERATURE CITED

1. B. V. Ioffe and V. A. Chernyshev, Dokl. Akad. Nauk SSSR, 214, 336 (1974).
2. J. Boyer, in: Heterocyclic Compounds [Russian translation], seventh edition, Mir, Moscow (1965), p. 325.
3. M. R. Atkinson and J. B. Polya, J. Chem. Soc., 141 (1954).