DIRECT IODINATION OF 1-ALKYLTETRAZOLES, A CONVENIENT METHOD FOR PREPARATION OF 1-ALKYL-5-IODOTETRAZOLES

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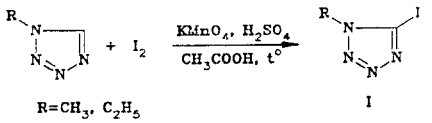
Iodine can be introduced into the 5 position of the tetrazole ring by the reaction of various 5-R-tetrazoles (R=NH_2, CH_3CO [1], CH_3COOHg [2], lithium [3]).

Using 1-methyl- and 1-ethyltetrazoles as examples, we have shown that 1-alkyltetrazoles, like aromatic carbocycles [4], undergo direct iodination in the presence of the $KMnO_4$–H_2SO_4 oxidizing system and that this reaction can be used as a convenient method for the synthesis of the corresponding 5-iodo derivatives:



The maximum yield of compounds I is attained when the reaction is carried out in 80% acetic acid. The use of the more concentrated acid decreases the yield of iodotetrazole, which corresponds to the concepts of the iodination mechanism [4].

To a solution of 2.07 g (0.025 mole) of 1-methyltetrazole in 80 ml of 80% CH_3COOH were added, with stirring, 6.35 g (0.025 mole) of finely triturated iodine, 5.1 g (0.03 mole) of $KMnO_4$, and 3.5 ml of concentrated H_2SO_4. The mixture was stirred for 4 h on a boiling water bath and filtered hot. The residue on the filter was washed with hot water, and the filtrate was evaporated in vacuo.

5-Iodo-1-methyltetrazole. By recrystallizing the residue from water, we obtained 3.96 g (75%) of 5-iodo-1-methyltetrazole in the form of slightly yellowish acicular crystals with mp 95-96°C [3]. Infrared spectrum (KBr): 1139, 1068, 1001 (ring), 680 cm^{-1} (C–I). Proton NMR spectrum (DMSO-D_6): 4.1 ppm (3H, singlet, CH_3).

5-Iodo-1-ethyltetrazole. This compound was obtained similarly in the form of colorless acicular crystals with mp 81.5-82.0°C (from a mixture of heptane with 2-propanol) in 55% yield. Proton NMR spectrum (DMSO-D_6): 1.45 (3H, triplet, CH_3); 4.38 ppm (2H, quadruplet, CH_2).

The elemental analysis of compounds I correspond to the calculated analysis.

In the iodination of 1-phenyltetrazole under the above-described conditions, a mixture of iodine-containing substances, which could not be separated and identified, was obtained. Under the conditions that were studied, 2-alkyltetrazoles did not undergo iodination.

LITERATURE CITED

1. F. R. Benson and R. Elderfield (eds), Heterocyclic Compounds [Russian translation], Vol. 8, Mir, Moscow (1969), p. 38.
2. R. Stolle and Fr. Henke-Stark, J. Prakt. Chem., 124, 261 (1930).
3. R. Raap, Can. J. Chem., 49, 2139 (1971).
4. V. K. Chaikovskii and A. N. Novikov, Zh. Prikl. Khim., 57, 134 (1984).

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