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# SYNTHESIS OF MESOIONIC 3-ARYL- AND 3-HETARYL-1,2,3,4-OXATRIAZOL-5-ONES

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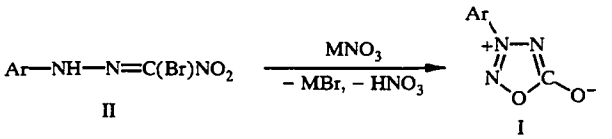
The mesoionic 3-R-1,2,3,4-oxatriazol-5-ones (3-R-1,2,3,4-oxatriazolium 5-olates, 3-R-azasydnones) present significant interest due to their antihypertensive activity [1]. However, the existing range of 3-arylazasydnones (I) is fairly limited. Thus, 3-hetarylazasydnones have been unknown until the present time. We found a method for the synthesis of (I) consisting in the reaction of bromonitroformaldehyde N-arylhydrazones (II) with alkali metal nitrates or ammonium nitrate in DMF or acetonitrile at ~20°C for several hours. It was communicated in the work [2] that the reaction of the hydrazones (II) (Ar = $C_6H_5$ and substituted $C_6H_5$) with $NaNO_3$ in DMF results in the formation of products of the substitution of the bromine atom by the nitrate grouping. However, not in one case did we find such compounds. The method allows the synthesis not only of the compounds (I) with various aryl ($C_6H_5$, p-$CH_3C_6H_4$, m-$CH_3OC_6H_4$, p-$BrC_6H_4$, p-F, and p- and m-$NO_2C_6H_4$) substituents, described in the literature [1, 3], but also hetarylsydnones. The last were shown using the examples of 3-(4-nitropyrazol-3-yl)azasydnone (Ia) and 3-(1,2,4-triazol-3-yl)azasydnone (Ib).




II I

Spectral indications allowing the reliable identification of (I) are as follows. The IR spectrum has a very strong band (usually as a doublet) at ~1800 $cm^{-1}$ (C–$O^-$), and the $^{17}O$ NMR spectrum has a characteristic narrow signal with the chemical shifts (from $H_2O$) of ~220 ppm (C–$\underline{O}^-$), as well as a broad signal at ~360-370 ppm ($O_{cyclic}$). The mass spectrum has the signal of the fragment $[M - NO]^+$.

Compound (Ia) has the mp 176-178°C (decomp.). The yield is 93%. The IR spectrum (pressed KBr, $cm^{-1}$) is as follows: 1345, 1540 ($NO_2$), 1790 (C–$O^-$), and 3300 (NH). The $^1H$ NMR (acetone-$D_6$) is characterized at 9.15 ppm (s, $C_{(5')}$–$\underline{H}$). The $^{13}C$ NMR (acetone-$D_6$) is as follows: 129.19 ppm (s, $C_{(4')}$), 133.16 ppm (d, 203.3 Hz, $C_{(5')}$), 136.35 ppm (s, $C_{(3')}$), and 165.93 ppm (s, $\underline{C}$–$O^-$). The $^{14}N$ NMR (acetone-$D_6$, from $CH_3NO_2$) is as follows: −23.03 ppm ($C_{(4')}$–$\underline{N}O_2$) and −83.03 ppm ($N^3$). The $^{17}O$ NMR ($CD_3CN$, from $H_2O$) is as follows: 225.2 ppm (C-$\underline{O}^-$), 369.6 ppm ($O_{cyclic}$), and 597.9 ppm ($N\underline{O}_2$). Found, %: C 24.5, H 1.2, and N 42.1. $C_4H_2N_6O_4$. Calculated, %: C 24.2, H 1.0, and N 42.4. Compound (Ib) has the mp 182°C (decomp.). The yield is 73%. The IR spectrum (pressed KBr, $cm^{-1}$) is as follows: 1815 (C–$O^-$) and 3300 (NH). The $^1H$ NMR (DMSO-$D_6$) is characterized at 9.00 ppm (s, C$\underline{H}$). The $^{17}O$ NMR ($CD_3CN$, from $H_2O$) is as follows: 221.0 ppm (C–$\underline{O}^-$) and 363.9 ppm ($O_{cyclic}$). Found, %: C 24.02, H 1.48, and N 54.38. $C_3H_2N_6O_2$. Calculated, %: C 23.38, H 1.30, and N 54.55.

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