CONVERSION OF AN AZIDO GROUP TO AN AMINO GROUP IN THE REACTION OF 1-R-3-NITRO-5-AZIDO-1,2,4-TRIAZOLES WITH ALIPHATIC AMINES

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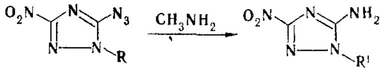
Replacement of a nitro group or a halogen atom in the 5 position of the ring by nucleophilic agents with different natures is widely used in the modification of the structure of 1,2,4-triazole derivatives. In particular, the reaction of 1-methyl-3,5-dinitro-1,2,4-triazole with aliphatic amines leads to the formation of the corresponding 5-amino derivatives [1]. However, an attempt to subject 1-R-3-nitro-5-azido-1,2,4-triazoles to similar reactions led instead to reduction of the azido group to give 3-nitro-5-amino-1,2,4-triazole derivatives (IV–VI):



I–III IV–VI

I, IV $R=R'=CH_3$; II, V $R=R'=CH_2COOH$; III $R=CH_2COOCH_3$; VI $R'=CH_2CONHCH_3$

Thus amino derivatives IV–VI, which were crystallized from ethanol, were precipitated with an equal volume of water when 0.025 mole of 1-R-3-nitro-5-azido-1,2,4-triazole (I–III) was added in portions to 15 ml of a 25% aqueous solution of methylamine (0.12 mole) at 40–50°C 3–5 h after cooling and acidification of the reaction mixture to pH 2 with hydrochloric acid. Compound IV was isolated by extraction with ethyl acetate. This method was used to obtain 1-methyl-3-nitro-5-amino-1,2,4-triazole (IV), with mp 253–254°C, in 82% yield; 3-nitro-5-amino-1,2,4-triazol-1-ylacetic acid (V) with mp 232–233°C [PMR spectrum: 4.90 (s, 2H, CH_2) and 7.20 ppm (s, 2H, NH_2)]; 3-nitro-5-amino-1,2,4-triazol-1-ylacetic acid methylamide (VI) with mp 278–279°C [PMR spectrum: 4.75 (s, 2H, CH_2), 7.10 (s, 2H, NH_2), 2.70 (s, 3H, CH_3), and 8.10 ppm (s, 1H, NH)].

1-R-3-Azido-5-R-1,2,4-triazoles are not reduced by amines under these conditions. Products of substitution in the 5 and 3 positions were not detected in a single case.

Reduction takes place when methyl-, dimethyl-, and triethylamine are used, and the use of the less basic ammonia and ethyleneimine leads to recovery of the starting substance. The reaction is probably a process of the addition-cleavage type with preferred attack by the nucleophile on the terminal nitrogen atom of the azido group rather than on the ring carbon atom to which it is bonded. The unusual fact of the reduction of an azido group by amines was recently noted in the pyridine series [2].

The analytical and spectral data (the IR spectra) for the compounds obtained are in agreement with the adopted structures.

LITERATURE CITED

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