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AMIDINES IN THE SYNTHESIS OF TETRAZOLES

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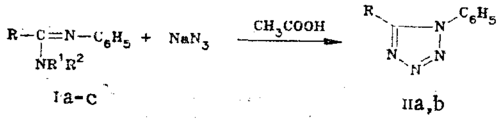
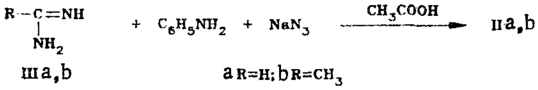
Amidines are widely used in the synthesis of nitrogen-containing heterocycles [1]; however, their use for the preparation of tetrazoles is unknown. Only the conversion of arylamidines under the influence of nitrous acid to give the so-called dihydroxytetrazotic acid has been described. The potassium salt of the latter is reduced by sodium amalgam to give a 5-substituted tetrazole in very low yield [2]. We have found that substituted amidines Ia-c react with sodium azide in acetic acid to give 1-phenyltetrazoles (IIa,b):



I a $R=R^1=H$, $R^2=C_6H_5$; b $R=H$, $R^1=R^2=CH_3$; c $R=CH_3$, $R^1=H$, $R^2=C_6H_5$; II a $R=H$; b $R=CH_3$

The reaction takes place at 90-100°C and gives the products in 45-60% yields after 3 h. In the case of amidine Ia it was shown that 2 moles of tetrazole IIa (90% yield) are formed when the reaction is carried out in the presence of an equimolar amount of ethyl orthoformate per mole of the amidine.

Since one of the methods for the preparation of Ia-c is transamination of unsubstituted amidines IIIa,b by primary amines [3], one might have assumed that amidines IIIa,b would act as the one-carbon component in a heterocyclization reaction via the scheme



$$\underset{\text{IIIa,b}}{\underset{NH_2}{R-\overset{}{C}=NH}} + C_6H_5NH_2 + NaN_3 \xrightarrow{CH_3COOH} \text{IIa,b}$$

a $R=H$; b $R=CH_3$

This reaction proceeds under the same conditions as in the preceding case and gives IIa,b in 45-65% yields.

The utilization of amidines, the synthesis of which can be accomplished by various pathways [1], significantly expands the source of 1- and 1,5-substituted tetrazoles.

A 0.8-mole sample of glacial acetic acid was added with stirring to a mixture of 0.1 mole of amidine Ia-c in the form of the acetate, methylsulfate, or free base and 0.12 mole of sodium azide, and the mixture was refluxed on a water bath for 2.5-3 h. The mixture was then cooled and filtered, and the filtrate was evaporated in vacuo. The residue was treated with 150-200 ml of a 3% solution of HCl, and the liberated oil (IIa or IIb) was crystallized in a refrigerator for 3-4 h.

The synthesis was carried out similarly starting from amidines IIIa,b, except that 0.12 mole of aniline was added after the NaN_3 was introduced.

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Compound IIa had mp 64-65°C (from 2-propanol) [2]. PMR spectrum (d_6-DMSO): 9.97 (1H, s, 5-H) and 7.36-7.64 ppm (5H, m, C_6H_5). Compound IIb had mp 97-98°C (from 2-propanol) [2]. PMR spectrum (d_6-acetone): 8.28 (5H, m, C_6H_5) and 2.66 ppm (3H, s, CH_3).

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