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SIMPLE METHOD FOR N-ALKYLATION OF 5-R-TETRAZOLES USING tert-BUTANOL

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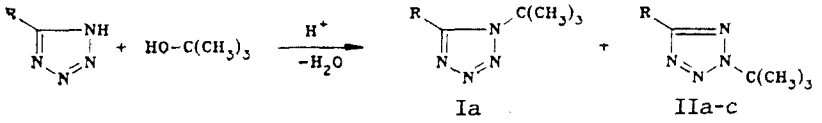
UDC 547.796.1.04

Direct tert-butylation of the pyrrole nitrogen atom in heterocycles occurs rarely [1] and is generally performed by an indirect method. Hence 1-tert-butyltetrazoles are obtained by decomposition of the gem-diazine t-Bu-C$(N_3)_2$Ph [2], reaction of methyl tert-butyl ketone with trimethylsilylazide [3], and by treating N-tert-butylacetonitrilium salts with sodium azide [4]. 5-Substituted tetrazoles can be tert-butylated by reaction with tert-butanol and dicyclohexylcarbodiimide [5]. However, this has been little applied because of its length and the need for careful adherence to numerous conditions.

We now show how direct tert-butylation of 5-R-tetrazoles can be achieved with tert-butanol and azeotropic distillation to eliminate water.



Ia IIa-c

I, II a R=CH_3, b R=C_6H_5, c R=CF_3

The PMR and ^{13}C NMR spectroscopy show that reaction of tert-butanol with 5-methyltetrazole gives a mixture of the 1- and 2-tert-butyl isomers Ia:IIa in the ratio 1:5. In contrast, reaction with 5-phenyl- and 5-trifluoromethyltetrazoles only yields the 2-isomers IIb and IIc. This agrees with the proposed effect of a 5-substituent on tetrazole ring alkylation [1].

A solution of tert-butanol (3.7 g, 50 mmoles) in chloroform (15 ml) was treated with concentrated H_2SO_4 (5-6 drops) and the 5-R-tetrazole (25 mmoles) and refluxed using a Dean and Stark apparatus until water (0.45 ml) had been removed. The product was diluted with chloroform (85 ml) and washed with Na_2CO_3 solution until the wash liquid was alkaline, and then with water until neutral. The chloroform solution was dried over $MgSO_4$ and then distilled to give the N-tert-butyltetrazoles Ia, IIa-c.

1-tert-Butyl-5-methyltetrazole (Ia). According to [3, 4], mp = 76-77°C. PMR spectrum: 2.70 (3H, s, Me), 1.69 ppm (9H, s, t-Bu). Yield 14%.

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2-tert-Butyl-5-methyltetrazole (IIa). bp 74°C (17 mm Hg), n_d^{20} 1.4447. PMR spectrum: 2.44 (3H, s, Me), 1.70 ppm (9H, s, t-Bu). Yield 69%.

2-tert-Butyl-5-phenyltetrazole (IIb). bp 90°C (0.1 mm Hg), n_D^{20} 1.5337. PMR spectrum: 8.08-8.18 (2H, m, o-H), 7.46-7.56 (3H, m, m,p-H), 1.78 ppm (9H, s, t-Bu). Yield 98%.

2-tert-Butyl-5-trifluoromethyltetrazole (IIc). bp 56°C (13 mm Hg), n_D^{20} 1.3855. PMR spectrum: 1.79 ppm (9H, s, t-Bu). Yield 85%.

Elemental analytical data for C, H, and N agreed with that calculated. The PMR spectra of Ia, IIa-c were recorded in acetone-d_6 (100 MHz).

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CHICHIBABIN AMINATION OF 1,3-DIMETHYLLUMAZINE

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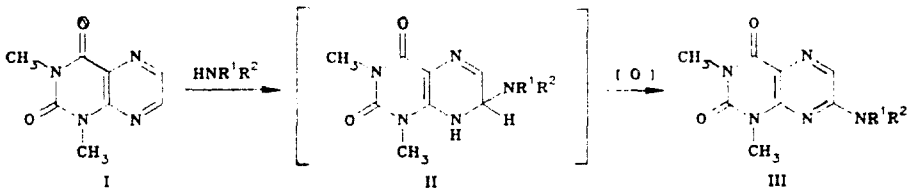
UDC 547.333'859'866

It is known that 1,3-dimethyllumazine (I) reacts with nucleophiles, in particular with alkali [1], hydrazine [2], and amines [3] at the amide $C_{(2)}$=O and $C_{(4)}$=O atoms with opening of the uracil nucleus. We now report the first example of nucleophilic substitution of hydrogen in the pyrazine ring of I with retention of the uracil fragment. It is shown that 1,3-dimethyllumazine (I) undergoes oxidative amination to give the 7-amino- and 7-alkylamino derivatives III in 20-35% yields.

A suspension of I in alkylamine (tert-butylamine, piperidine, morpholine) at 10-15°C was treated portionwise over 2-4 h with $[Ag(C_5H_5N)_2]MnO_4$ oxidant [4]. $KMnO_4$ cannot be used because of its insolubility in the indicated amines. Excess alkylamine was distilled off, the residue extracted with chloroform, and the product separated by column chromatography. The same reaction could not be carried out using liquid ammonia, evidently because of its low boiling point. However, amine IIIa could be prepared using potassium amide in liquid ammonia with oxidation of the adduct IIa using potassium permanganate.



a $R^1=R^2=H$; b $R^1=H$, $R^2=C(CH_3)_3$; c NR^1R^2 = piperidinyl; NR^1R^2 = N-morpholinyl

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