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# REACTION OF SILYLURACILS WITH ALDEHYDES — A METHOD FOR THE SYNTHESIS OF SILOXYMETHYLURACILS

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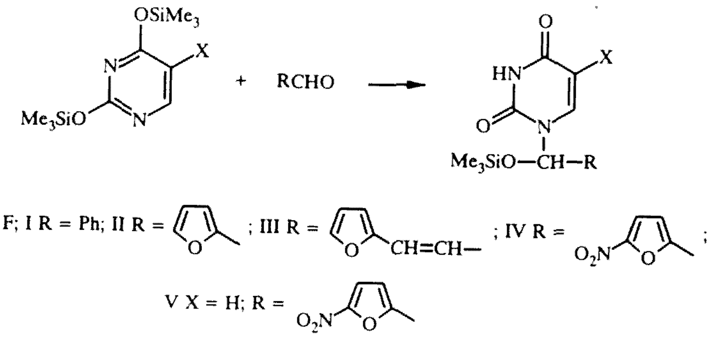
It was shown recently that trimethylsilylamides react with aldehydes in boiling chloroform or at room temperature in the presence of trimethylsilyl triflate with the formation of 1-acylamino-1-(trimethylsiloxy)alkanes [1, 2]. The N-silylamides, e.g., bis(trimethylsilyl)formamide, thereby entered into the reaction significantly more readily than O-silylamides, and bis(trimethylsilyl)acetamide did not react at all. In order to explain the mechanism of the reaction, the presence of the imidate (O-silyl) form in the reaction mixture is assumed all the same.

We found that silylated uracils, i.e., compounds with the fixed imide $-N=C-OSi$ grouping, react readily with aromatic (benzaldehyde) and heteroaromatic (furfurol, 5-nitrofurfurol, furylacrolein) aldehydes in acetonitrile with the formation of α-siloxyamides.



As an example, we present the account of the reaction of 2,4-bis(trimethylsilyl)-5-fluorouracil with benzaldehyde.

The solution of 2.7 g (0.01 mole) of 2,4-bis(trimethylsilyl)-5-fluorouracil and 1.1 g (0.01 mole) of benzaldehyde in 20 ml of acetonitrile is prepared prior to the addition of 1.7 g of potassium iodide. The mixture is stirred at room temperature for 24 h. The residue is filtered off and washed with acetonitrile. The solvent is evaporated. Chloroform is added to the residue, and the mixture is stirred, and then filtered through a layer of silica gel. After the evaporation of the solvent, the residue is recrystallized from the 1:2 mixture of hexane—benzene. The yield of 0.45 g of 1-(α-trimethylsiloxybenzyl)-5-fluorouracil (I) is obtained. It has the mp 135-137°C, and the $R_f$ 0.74 (the 1:8 mixture of acetone—chloroform). The PMR spectrum ($CDCl_3$, TMS), given as the δ, is as follows: 0.22 ppm (9H, s, $SiMe_3$), 7.12 ppm (1H, d, CH, $^4J = 0.8$ Hz), 7.23 ppm (1H, d, $H_{(6)}$, $^3J_{HF} = 6.0$ Hz), 7.42 ppm (5H, s, Ph), and 9.0 ppm (1H, broad s, NH).

In the same way, 5-nitrofurfurol reacts readily at room temperature. Some heating was required in the case of the remaining aldehydes. The trimethylsiloxy derivatives are characterized by the melting points. Compound (II) has the mp 115-116°C. Compound (III) has the mp 150-151°C. Compound (IV) has the mp 165-168°C. Compound (V) has the mp 196-198°C. An excess of 5-nitrofurfurol also gave the 1,3-bis-derivative with the mp 116-118°C.

It can be assumed that the reaction proceeds via the six-membered intermediate complex in which the nitrogen atom attacks the carbon, and the silyl group attacks the oxygen atom of the carbonyl group.

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