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DIHYDROSILAAZAANTHRACENES

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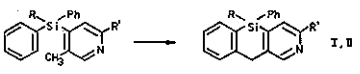
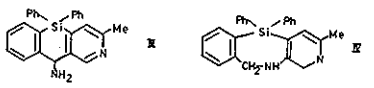
Synthesis of new heterocyclic systems - dihydrosilaazaanthracenes I and II (yield 25—30%) has been performed by dehydrocyclisation of 2,5-dimethyl-4-triphenylsilyl-and 3-methyl-4-methyldiphenylsilylpyridines at 530—540° on dehydrogenation catalyst.



I R = C_6H_5, R' = CH_3; II R' = H, R = CH_3

Increase or decrease of dehydrocyclisation temperature specifically decreases the yield of I and II. I is obtained from 1,2,5-trimethyl-4-triphenylsilyl- Δ^4-piperidiene in 1% yield. Structures of I and II have been confirmed by IR, NMR and Mass-Spectroscopy.

Oxidation of I and II resulted in the yield of silaazaanthrones. Condensation of I with excess of benzaldehyde gave trans-2-styryl-9,9-diphenyl-9-sila-9,10-dihydro-3-azaanthracene which was subsequently oxidised to 9,9-diphenyl-9-sila-9,10-dihydro-3-azaanthrone-2-carboxylic acid.



Reduction of oxime 2-methyl-9,9-diphenyl-9-sila-9,10-dihydro-3-azaanthrone by $LiAlH_4$ in THF produced compounds III and IV.

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STUDIES ON THE REACTIVITY OF NITRAMINOPYRIDINES

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Nitraminopyridines are well known as the reagents. Their nitramino groups can be substituted with all the halogen atoms, hydroxy, and hydrazino groups. We have attemped to extend the range of the application of nitraminopyridines in the chemical syntheses using the fact that the ionized nitramino group is the ortho- and para- directing, electron donating substituent ($\sigma_{p-NNO_2^-} = -0.43$, $\sigma_{m-NNO_2^-} = 0.000$). Thus we have shown that both 2- and 4- nitraminopyridine anions can be monochlorinated and monobrominated by means of chlorine and bromine, respectively. These reactions proceed via the formation of corresponding N-halogeno nitraminopyridines. The latest undergo rearrangement in the aqueous solution at the elevated temperature.

When 2-nitraminopyridine undergo acid catalyzed rearrangement in the conc. H_2SO_4 solution both 2-amino-5-nitro- and 2-amino-3-nitropyridines are formed. Our studies have shown that the process is of the mixed intra- and intermolecular character. The acid catalysis is specific in its nature. The rearrangement is of the first rate with respect to the substrates and the transition state is highly polar.

Electron donating substituents in the β-positions accelerate the rearrangement and the electron withdrawing groups slow down the process. The opinion that 3-substituted 2-nitraminopyridines rearrange more readily than their 5-substituted isomers is incorrect.

The isomer ratio of 2-amino-5-nitro- and 2-amino-3-nitropyridines which is 4 : 1 after the rearrangement in the conc. H_2SO_4 solution and the 68% aq $HClO_4$ solution can be influenced by the decrease of the concentration of the catalyzing acid. In more diluted acidic media this ratio changes up to 2 : 1. This is, however, accompanied by the decrease in both the yield and rate of the rearrangement. In the 80% aq. H_3PO_4 solution only 2-amino-3-pyridine is formed, however, with 5% yield. The temperature effects only the rate of the process and does not influence the isomer ratio.

The rearrangement of 2-nitraminopyridine in the $HClO_4$ solutions is accompanied by the chlorination. Thus 2-amino-3-nitro-5-chloropyridine is formed as the only product of the rearrangement. Since 2-nitraminopyridine anion can be either chlorinated in the 5-position, exclusively, it is to believe that 2-nitraminopyridine is chlorinated rather than the rearrangement product. The duplication of that reaction using the HIO_3 and H_5IO_6 solutions was unsuccessful.

The thermal decomposition of nitraminopyridines appears to be the process autocatalyzed by the proton with the varying ratio of isomers formed during the rearrangement. The thermal rearrangement of N-methylnitramines is very slow.

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AZAFLUORENES

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Existing information of these heterocyclic compounds is limited. In this report, dedicated to the chemistry of azafluorenes, the following objects used in the synthesis and study of azafluorenes are represented:

1. Synthesis of substituted pyridines from γ-piperidons. Conversion of γ-piperidons into γ-piperidols, dehydration, dehydrogenation, N-dealkylation of these to pyridine bases.

2. Catalytic dehydrocyclisation of substituted pyridines resulting in 2-, 3- and 4-azafluorenes.3.Reduction of 2-azafluorenes to isomeric indano [2,1-c]piperidines.4.Synthesis of 3-styryl-2-azafluorene isomers.5.Synthesis and configuration of isomers of benzopyridofulvenes.6.Pyridyl substituted azafluorenes.7.Zwitter ions of azafluorenes and their interaction with acetylenedicarboxylic ether.8.Azafluorenes in the synthesis of indenoindolizines. 9.Spiro compounds with azofluorene fragment.10.Azafluorenes in the synthesis of new heterocyclic systems - azafluorentens. The following research has been conducted by the collaborators and research scholars of the Department of Organic Chemistry Patrice Lumumba People's Friendship University Moscow.

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CONVERSION OF PYRIDO[2,3-d]PYRIMIDINES INTO SOME OTHER HETEROCYCLES

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The synthesis of 4-aminopyrido[2,3-d]pyrimidine-3-oxide (II) from I (R = H or CH = NOH) or III is described. The oxide (II) when treated with acetic anhydride and then hydrolyzed, gives the oxadiazolyl compound (IV), obtainable also from I upon acetylation and heating the N-acetoxy derivative. The 3-oxide when treated with N,N-dimethylformamide dimethylacetal gives the corresponding 4-N,N-dimethylaminomethyleneamino compound which upon treatment with hydroxylamine gives the oxadiazolyl derivative (V). This, when treated with polyphosphoric acid is transformed into the s-triazolo(1,5-a)pyridine derivative (VI) which upon heating gives the corresponding cyano derivative (VII).