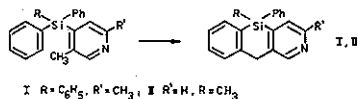


LE II 8

DIHYDROSILAAZAANTHRACENES

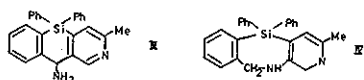
 A. V. Varlamov*, N. S. Prostakov, Navin Saxena, A. M. Klochkov
 Patrice Lumumba People's Friendship University, Moscow

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-methyl-diphenylsilylpyridines at 530-540° on dehydrogenation catalyst.



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 -piperidine 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 siloazaanthrones. 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 LiAlH₄ in THF produced compounds III and IV.

LE II 9

STUDIES ON THE REACTIVITY OF NITRAMINOPYRIDINES

 Eworyst E. Pasternak, Antoni Thomas, Piotr Tomosik*
 and Romuald Zalewski

 Department of Chemistry, Higher School of Engineering,
 45-056 Opole, Poland.

 Department of Organic Chemistry, Pedagogical University,
 42-201 Częstochowa, Poland.

 Institute of the Product Determination, Academy of Economics,
 60-967 Poznań, Poland.

Nitraminopyridines are well known as the reagents. Their nitramino groups can be substituted with all the halogen atoms, hydroxy, and hydrazino groups. We have attempted 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 (σ_p - NNO_2 = -0.43, σ_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. H₂SO₄ 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. H₂SO₄ solution and the 68% aq HClO₄ 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. H₃PO₄ 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 HClO₄ 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 HIO₃ and H₅IO₆ 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.

LE II 10

AZAFLUORENES

N. S. Prostakov

Patrice Lumumba People's Friendship University, Moscow

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 indenoid alkaloids.
 9. Spiro compounds with azafluorene 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.

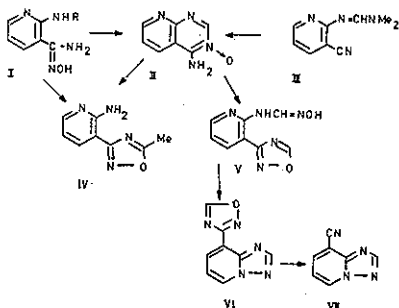
LE II 11

CONVERSION OF PYRIDO(2,3-d)PYRIMIDINES INTO SOME OTHER HETEROCYCLES

B. Verček*, B. Stanovnik, and M. Tišler

 Department of Chemistry, University of Ljubljano, Ljubljano,
 Yugoslavia

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).



The structures of compounds follow from analytical, spectroscopic and X-ray data. Some other transformations, such as reduction, deoxygenation and cyclizations will be presented.

LE II 12

VILSMEIER-HAACK REACTION OF 5-AMINO-PYRAZOLE DERIVATIVES

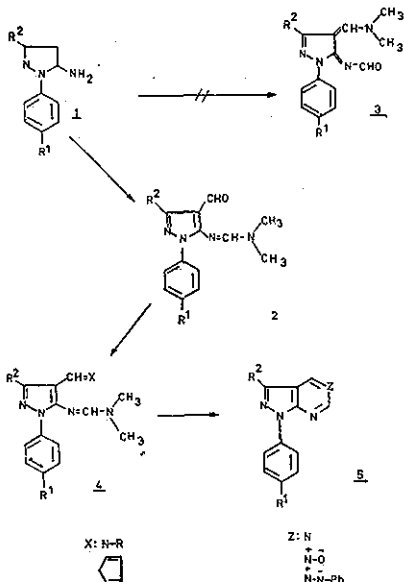
Antal Simay* and Kálmán Takács

Research Laboratory of Chinoïn Pharmaceutical and Chemical Works H-1045 Budapest, Tó u. 1-5.

Vilsmeier-Haack reaction of some 1-substituted 5-amino-pyrazoles (1) has been reported by several groups of authors. The products of the reaction have been characterised either by structure 2 (1,2) or 3 (3).

In order to elucidate the above mentioned structural problem we reinvestigated the reactions of 1-substituted and 1,3-disubstituted 5-amino-pyrazoles with dimethyl-formamide — phosphoryl-chloride reagent.

We have found that reactions of 1 and DMF-POCl₃ result in the formation of compounds 2 only, independently of the character of R₁ and R₂ substituents. No protection of the 5-amino



group could be achieved by acylation. Vilsmeier-Haack reaction of 5-acylamino-pyrazoles is accompanied by acyl-splitting and also in these cases compounds 2 are obtained.

Structure 2 was proved by the spectral and chemical properties of the products. The formyl group of 2 could be selectively condensed with nitrogen bases (i. e. phenyl-hydrazine etc.) and CH-acid compounds, leading to pyrazole derivatives 4. Certain representatives of compounds 4 (X = NR) could be cyclized and pyrazolo[3,4-d]pyrimidines (5) were obtained. In some cases spontaneous second-step cyclisation was observed. The mechanism of the reactions mentioned above will also be discussed.

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- 3) Kvitko, I. J., Loginova, T. M.; Zh. Obshch. Khim. 10 1088 (1974)

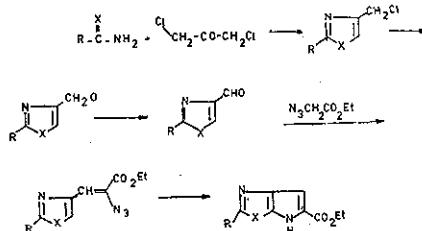
LE II 13

SYNTHESIS OF PYRROLO[3,2-d]SELENAZOLE AND PYRROLO [3,2-d]THIAZOLE. TWO NOVEL HETEROCYCLES

A. Shafiee* and A. Mazloomi

Department of Chemistry, College of Pharmacy, Tehran University, Tehran/Iran

As a part of a program designed to expand the chemistry of fused pyrrole heterocycles, a method was developed for the synthesis of pyrrolo [3,2-d]selenazoles and pyrrolo [3,2-d]thiazoles as it is shown below.



R = H, CH₃, C₆H₅; X = S
R = C₆H₅, p-ClC₆H₄, p-BrC₆H₄, β-MeC₆H₄, p-CH₃OC₆H₄, C₆H₅S-; X = Se

The chemistry and structure elucidation of these new heterocycles will be discussed.

LE II 14

THE SYNTHESIS OF 3-SUBSTITUTED AND 3,5-DISUBSTITUTED DERIVATIVES OF 1,2,4-TRIAZOLE

Tomáš Vaněk, Vlasta Velková and Jiří Gut

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague 6

Thermal condensation of thioamides I with acylhydrazides II affords N1-acylamidrazones III which cyclize to triazoles IV on heating above their melting point. The reaction can be carried out in one step, without the isolation of the intermediate III.

