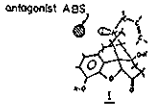

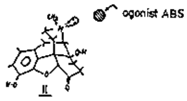

PO 37

SYNTHESIS OF 1-ALKYL- and 1-ARYL-3-(2-PYRIDYL) ISOQUINOLINES

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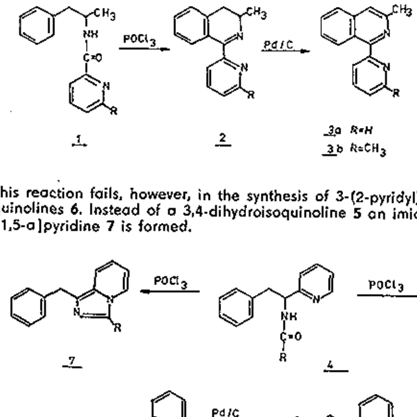
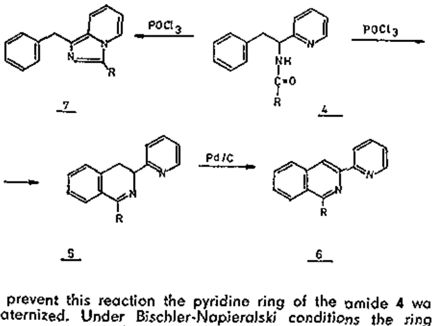
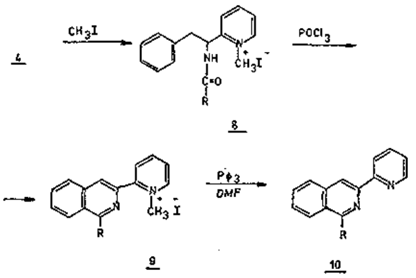
In an investigation concerning the anti-Mycoplasma activity of compounds possessing the 2,2'-bipyridyl skeleton it was found that ortho substitution has a pronounced positive effect[1]). To study the influence of substitution on the anti-Mycoplasma activity in more detail a series of 1-alkyl- and 1-aryl-3-(2-pyridil)isoquinolines was prepared. For the synthesis of isoquinolines the Bischler-Napieralski reaction is often applicated. In this way the preparation of the 1-(2-pyridyl)isoquinolines **3a** and **3b** indeed could be accomplished.



This reaction fails, however, in the synthesis of 3-(2-pyridyl)isoquinolines **6**. Instead of a 3,4-dihydroisoquinoline **5** an imidazo [1,5-a]pyridine **7** is formed.



To prevent this reaction the pyridine ring of the amide **4** was quaternized. Under Bischler-Napieralski conditions the ring-closure now could be effectuated, leading directly to the isoquinoline **9**. After demethylation the desired product **10** could be isolated.



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B. M. ANTIĆ, H. van der GOOT, W. TH. NAUTA, S. BALT, M. W. G. de BOLSTER, A. H. STOUTHAMER, H. VERHEUL and R. D. VIS, Eur. J. Med. Chem. 12, 573-575 (1977).

PO 38

DEVELOPMENTS IN CHEMISTRY OF NITROGEN ANALOGUES OF FLUORENE

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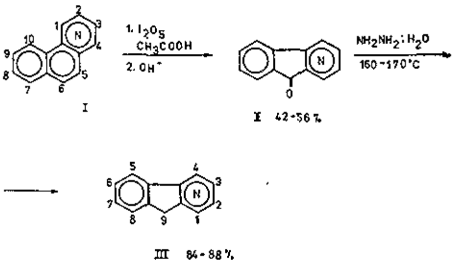
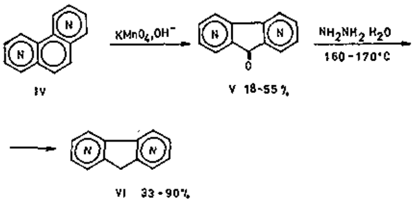
In connection with the considerable current interest in the chemistry and biological activity of some azafluorenone and azafluorene derivatives we report a convenient synthesis of this class of compounds and results of their N-alkylation and oxidation. Monoazaphenanthrenes (I) and phenanthrolines (IV) were used as starting materials. Treatment of 1- and 4-azophenanthrene with I_2O_5 in acetic acid afforded azaphenanthrene-5,6-diones which were converted to 4- and 1-azafluorenones (II) respectively, by rearrangement in alkaline medium. The next step was reduction of (II) with hydrazine to monoazofluorenes (III).



Phenanthrolines (IV) were oxidized directly by means of permanganate in alkaline medium to 1,5-, 2,5-, 4,5- and 1,8-diazafluorenones (V) which were reduced with hydrazine to give diazafluorenes (VI).



Under the reduction conditions 4-aza-, 2,5- and 4,5-diazafluorenones yielded besides azafluorenes also condensation products — 9,9'-bis- azofluorenes.
It was established that azafluorenones (III, VI) undergo N-methylation with methyl iodine to give only monomethyliodines with 39 to 98% yield. The kinetic data give evidence that the nitrogen atoms of azafluorenones are less active toward N-alkylation than those of azafluorenes. This is due to the negative electromeric effect of the carbonyl group. We confirmed the lower susceptibility of the 4-N atoms to N-methylation than of the other N atoms; this fact can be explained by the shielding effect of the 5-H atoms.
The azafluorenones were oxidized with hydrogen peroxide in an acetic acid — benzene mixture. Some of the diazafluorenone N-oxides were unstable in acidic media and oxidation had to be accomplished directly with hydrogen peroxide in the presence of Na_2WO_4. The monoazafluorenones under the same conditions were oxidized to azafluorenone N-oxides, but oxidation of diazafluorenes led first to diazafluorenones which then formed diazafluorenone N-oxides. Yields of N-oxides were 22 to 69%.
Bacteriological properties of most synthesized compounds were tested. The most interesting results have been obtainel for the 2,5-diazafluorenone-di-N-oxide and 1-azafluorenone-N-methyl-iodide.

PO 39

SYNTHESIS AND ANTIPARASITIC PROPERTIES OF IMIDAZO [1,5-a]-PYRIDINE DERIVATIVES

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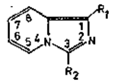
A number of new imidazo[1,5-a]pyridine derivatives (I) were prepared by different methods:



(I)

a) Cyclization of aminomethyl-2 pyridine derivatives to the fused ring system (I).
b) Electrophilic substitution at C-1 of (I).
c) Nucleophilic substitution at C-3 of (I).

The protozoocidal and anthelmintic activities of the imidazo-[1,5-a]pyridine derivatives (I) are reported.

PO 40

ALKYL DERIVATIVES OF AZAPHENANTHRENES

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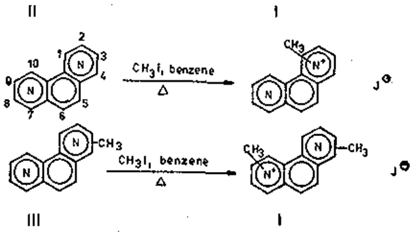
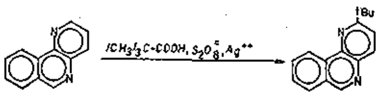
Since the N- and C-alkyl derivatives of polycyclic azines, and especially N-methyl iodies are receiving considerable attention as potential antineoplastic agents, we studied the synthesis and properties of the hitherto unknown alkyl azaphenanthrenes. N-methyl derivatives (I) were synthesides by direct alkylation of suitable azaphenanthrenes (II) or their methyl derivatives (III) in 77 to 98% yield.

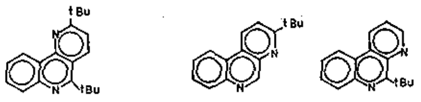


where N 1 or 4 as well as 1,5, 1,6, 1,7, 1,8, 1,10 4,6, 4,7 CH_3 1,2,3,4,8 or 9
The nitrogen ione electron pairs are shielded less by methyl dered N atoms (for instance in the 1 position), except in the case of 1,10-diazaphenanthrene, whose unexpectedly high reactivity is due to the absence of boat protons, as well as to the high electron density of the neighbouring nitrogen atoms.

The nitrogen ione electron pairs are shielded less by methyl groups than by protons in the boat position.
t-Butylation was performed on azaphenanthrenes using t-butyl radicals generated from pivalic acid in the presence of $S_2O_8^{=}$ and Ag^{++}ions.
For 1,5-diazaphenantherene:



1,6-Diazaphenanthrene gave 2,5-di-t-butyl derivative, and 4,6-diazaphenanthrene — a mixture of 3- and 5-mono-t-butyl derivatives (2 : 1). The yields were 26 to 42%.



It was found, that the substitution positions were those predicted by calculation of localization energy values for nucleophilic reactions; this result suggests nucleophilic character of t-butyl radicals. However, steric factors also had to be considered.
Some of N-methyl iodides, especially those derived from 1,10-diazaphenanthrene posses high antibacterial and antifungal activities.

PO 41

THE KNOEVENAGEL REACTION OF MALONONITRILE WITH SOME CYCLIC β-KETO ACIDS ANILIDES

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Department of Organic Chemistry of Jagiellonian University, Poland

As continuation of previous work on Knoevenagel's condensation of some cyclic β-keto acids anilides with compounds containing active methylene group the reaction of cyclopentan-2-one-1-carboxylic acid anilide (**1**) and cyclopentan-2-one-1,3-dicarboxylic acid dianilide (**5**) with malononitrile was investigated.

It was stated that the reaction of cyclopentan-2-one-1-carboxylic acid anilide (**1**) with malononitrile in presence of acetic acid in boiling benzene solution yielded 2-dicyanomethylene cyclopentane-1-carboxylic acid anilide (**2**).

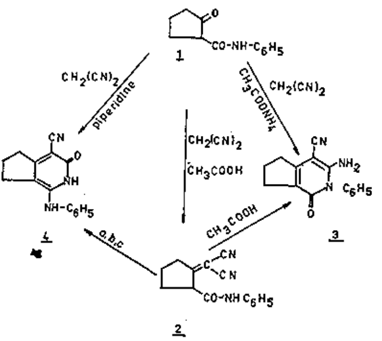
The condensation of anilide **1** with malononitrile in boiling toluene with acetic and ammonium acetate as catalyst yielded compound **3** isomeric with compound **2**. The structure of compound **3** was determined on the basis of spectral data and of its chemical properties as 1-cyano-2-amino-3-phenyl-4-oxo-3,4,6,7-tetrahydro-5-H-cyclopenta(c)-pyridine.

A different course of the reaction of anilide 1 with malononitrile has been observed when the reaction was carried out in presence of base catalyst. The reaction performed in boiling toluene solution with piperidine and pyridine afforded compound **4**, which has found to be isomeric with previously described compounds **2** and **3**. Compound **4** was also obtained by conversion of compound **2**:

a) in methanolic solution in presence of pipiridine and pyridine

b in boiling solution of sodium hydroxide

c) by prolonged boiling with water



On the basis of spectral data and chemical properties the structure 1-cyano-2-oxo-4-anilino-2,3,6,7-tetrahydro-5H-cyclopenta(c)-pyridine was assigned to compound **4**.

The condensation of cyclopentan-2-one-1,3-dicarboxylic acid dianilide (**5**) with malononitrile in boiling toluene solution with piperidine and pyridine or ammonium acetate and acetic acid afforded the same product: 2-dicyanomethylene cyclopentane-1,3-dicarboxylic acid dianilide (**6**).

All the proposed structures were supported by IR, ^{1}H-NMR and MS spectral data

PO 42

ALKYLATION OF 2-CYANAMINOBENZIMIDAZOLE AND ITS ALKYLATED DERIVATIVES

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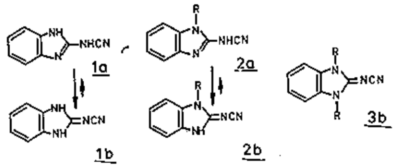
Alkylation of 2-cyanaminobenzimidazole **1** under various conditions led to mono and disubstituted products **2** and **3**.

IR and UV spectra revealed that compounds **3** possess a symmetrical structure of 1,3-dialkyl-2-benzimidazolidenocyanamide 3b (IR: CN band at 2170 — 2200 cm^{-1}, shifted toward lower frequencies in consequence of coupling between cyano and imino group $\rangle C = N - C \equiv N$. UV: maxima at 240, 290 and 295 nm).



Analogous tautomeric form is also predominant in the case of the parent compound **1b** and its monosubstituted derivatives 2b, position of the alkyl group in the latter being unequivocally established on chemical way.

An evidence of participation of tautomeric forms **1a** and **2a** in the structure of compounds 1 and 2 was provided by the synthesis of tricyclic derivative **4**:

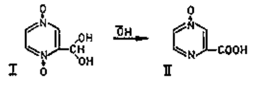
PO 43

THE OXIDATION-REDUCTION REACTION OF QUINOXALINE-2- AND 1,5-NAPHTHYRIDINE-2-ALDEHYDE N-OXIDES AND THEIR HYDRATES

A. S. Elina, I. S. Musatova*, R. M. Titkova, E. A. Trifonova

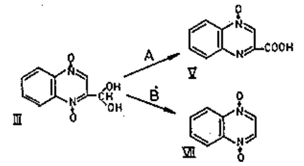
S. Ordzhonikidze All-Union Chemical-Pharmaceutical Research Institute, Moscow, USSR

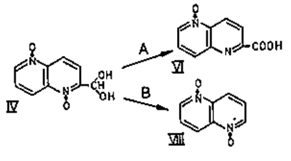
It was shown previously that pyrazine di-N-oxide, replaced by a dihydroxymethyl group at the carbon next to the oxidised nitrogen of the cycle (hydrate of pyrazine-2-aldehyde di-N-oxide, I) undergoes oxidation of its dihydroxymethyl group to carboxy group and deoxidation of the neighbouring nitrogen to form pyrazine-2-carboxylic acid 4-N-oxide (II) under the attack of strong or weak nucleophiles (reaction A)[1].



In order to develop investigations in this direction, the oxidation-reduction reactions of the hydrates of quinoxaline-2- and 1,5-naphthyridine-2-aldehydes di-N-oxides (III and IV respectively) have been studied.

It was found that in contrast to I, compounds III and IV, under the action of nucleophilic reagents (NaHCO$_3$ or NaOH solutions) undergo two types of reactions depending on pH: re-





action A to form 2-carboxyquinoxaline 4-N-oxide (V) or 2-carboxy-1,5-naphthyridine 5-N-oxide (VI) respectively and reaction B to form di-N-oxides of unsubstituted quinoxaline or 1,5-naphthyridine (VII and VII).

Quinoxaline-2-aldehyde isolated in the form of a carbonyl compound mainly undergoes reaction B changing to quinoxaline-di-N-oxide.

The optimum pH ranges for reactions A and B were investigated and a possibility of these reactions proceeding simultaneously shown.

The differences in the behavior of quinoxaline and 1,5-naphthyridine di-N-oxides derivatives were revealed.

The transformations of diethylacetal quinoxaline-2-aldehyde di-N-oxide proceeding in the presence of alkaline reagents were studied.

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1) A. S. Elina, I. S. Musatova, G. P. Syrova „Chemistry of the Heterocyclic Compounds", 1972, 9, 1275—1280.

PO 44

POLAROGRAPHIC REDUCTION OF ISOXAZOLES AND THEIR AZAANALOGS IN ANHYDROUS DIMETHYLFORMAMIDE

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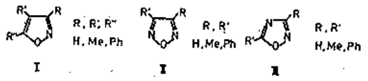
The polarographic behavior of substituted isoxazoles (I) and their azaanalogs (II, III)



was studied in anhydrous dimethylformamide against the background of quarternary ammonium salts. It was shown that the phenyl substituted compounds I possess polarographic activity and the first irreversible two-electron wave corresponds to N-O-bond rupture to form the dianion which is capable of being reduced only in a more negative potential range. In an accessible potential range, four-electron reduction of the derivatives I is likely, with the $E_{1/2}$ value of the second wave depending on the cation nature of the background. Complete saturation of multiple bonds after N-O-bond rupture requiring six electrons can be realized in excess proton donors(benzoic acid).

While reducing the derivatives II and III the first stage also involves two-electron irreversible rupture of N-O-bond. Isoxazole analogs are reduced substantially easier in all cases. The reduction depth of oxadiazoles studied is determined by their structure and protonation rate of intervening particles formed. In the accessible potential region oxadiazol III(R = R' = Me) is capable of accepting two electrons, oxadiazoles II(R = R' = Me), III(R = R' = Ph), III(R = Ph, R' = Me) and III(R = Me, R' = Ph) — four electrons. Complete molecular reduction involving eigth electrons takes place only in the case of oxadiazole II(R = R' = Ph).

In the series of isoxazole I and oxadiazole II and III derivatives greater conjugation of the phenyl ring in the fifth position facilitates the reduction as compared to the corresponding 3-substituted compounds. The replacement of methyl substituents by phenyl ones in disubstituted oxadiazoles III leads to facilitating the reduction/$\Delta E^{1/2}$ of the first waves — 970 mV whereas the analogous effect for oxadiazoles II is 540 mV which is determined by partially broken conjugation due to space interaction of benzene rings in case of 3,4-diphenyl-1,2,5-oxadiazole.

PO 45

SYNTHESIS AND REACTIONS OF ARYLOXYFURAN DERIVATIVES

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A general method of preparing aryloxyfuran derivatives has been developed.

The aryloxyfuran formulation according to the method of Vilsmeier yields 5-aryloxyfurfurals, which were further transformed to 5-aryloxy-2-methylfurans by the Kishner-Wolff reduction.

The corresponding amides were obtained on the basis of the aryl esters of 5-aryloxypyromucic acids and then turned into 2-aminomethyl-5-aryloxyfyrans by the reduction with $LiAlH_4$.

The aryl esters of aryloxypyromucic acids reacted with hydrazine-hydrate to give aryloxypyromucic hydrazides, which formed isopropylidene derivatives by the reaction with acetone.

The hermistatic activity of the compounds synthesized has been investigated

PO 46

THE REACTION OF ARYL- AND ARYLOXYFURANS WITH DIMETHYL ACETYLENEDICARBOXYLATE

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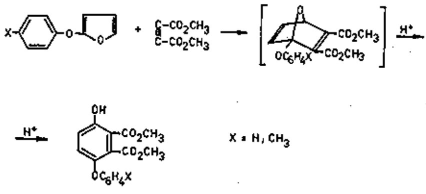
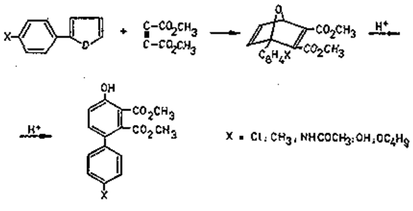
The diene synthesis of aryl- and aryloxyfurans with dimethyl acetylenedicarboxylate has been studied.

The interaction of arylfurans with acetylenedicarboxylic ester yields adducts, which undergo aromatization leading to the esters of hydroxybiphenyldicarboxylic acids.



The presence of electron-donating substituents in the benzene ring of arylfuran favourably affects the above mentioned reaction.

Aryloxyfurans undergo the Diels-Alder reaction with dimethyl acetylenedicarboxylate, giving adducts, which can be transformed by the action of acids to 1-hydroxy-4-phenyloxydicarboxylic acids.



Thus, the synthesis of not readily available esters of hydroxycarboxylic acids of the biphenyl and diphenyloxide series has been realized.

PO 47

SYNTHESIS AND TRANSFORMATION OF THE DERIVATIVES OF PYRROLO(3,2-d)PYRIMIDINE-7-ALDEHYDE

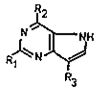
O. S. Kuptsova, N. E. Britikova, K. Yu. Novitskii

S. Ordzhonikidze All-Union Chemical-Pharmaceutical Research *Institute, Moscow, 119815, USSR*

The method of preparing pyrrolo(3,2-d)pyrimidine derivatives based on using of Vilsmeier reagent for pyrrolo cyclization in 5-amino-6-methylpyrimidines, has been found. 4-oxopyrrolo(3,2-d)pyrimidine-7-aldehyde (I), prepared in such a way from 4-oxo-5-amino-6-methylpyrimidine, was transformed to 4-chlorpyrrolo(3,2-d)pyrimidine (II).

In similar conditions during the cyclization of 2-phenyl-4-oxo-5-amino-6-methylpyrimidine the substitution of the oxo-group by chlorine to form 2-phenyl-4-chlorpyrrolo(3,2-d)pyrimidine-7-aldehyde (III) simultaneously proceeds. The nitril (IV) from the aldehyde (III) has been received.

The reaction of the nucleophilic substitution of the chlorine atom in compounds II and IV was investigated.



I. $R_1 = H$
$R_2 = O$
$R_3 = C\genfrac{}{}{0pt}{}{=O}{-H}$
II. $R_1 = R_3 = H$
$R_2 = Cl$

III. $R_1 = C_6H_5$
$R_2 = Cl$
$R_3 = C\genfrac{}{}{0pt}{}{=O}{-H}$
IV. $R_1 = C_6H_5$
$R_2 = Cl$
$R_3 = C\equiv N$

PO 48

NOVEL 2-BENZENESULFONAMIDO-4-AMINO-5-BENZYLPYRIMIDINES AND SOME OF THEIR REACTIONS

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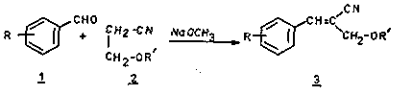
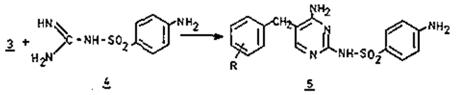
[2]University of K.L., H-4010 Debrecen, PF. 20.
[3]Medical University, H-4012 Debrecen, PF. 12.

In the EGYT *Pharmacochemical* Works purposeful research has been continuing for years on the field of chemotherapy. One of these important trends is to produce compounds having antibacterial activity. It is well-known, that in the therapy Trimethoprim (2,4-diamino-5-[3',4'5-'trimethoxybenzyl]-pyrimidine) shows synergism with sulfonamides.

We wanted to synthesize modified pyrimidine compounds including the sulfonamide-part on the pyrimidine-ring.

In the present work, the synthesis and several reactions of the new pyrimidine derivatives (**5—7**) are studied. Thus the suitable compounds were produced by the following synthesis route:

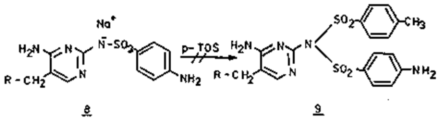




5 R = 3,4,5-MeO; **6** R = 3,4-MeO; **7** R = 3,4-methylenedioxy
R' = alkyl

Substituted benzaldehydes (1) were condensed with 3-ethoxypropionitril (2) in presence of sodium-methoxide during 12 hours, at reflux temperature and gave 2-(subst.-benzylidene)-3-methoxypropionitril (3). **3** was cyclized with sulfoguanidin (4) in presence of sodium-methoxide, in an autoclave during 16 hours at 100 °C. In this way we obtained N_1-(2-(4-amino-5-subst.benzyl)-pyrimidil)-p-aminobenzenesulfonamid (**5—7**).

The proton-activity of sulfonamid-NH- of our materials was studied. After preparing sodium salts of **5,6,7**, we live them reacted with p-toluenesulfonyl chloride (p-TOS) in organic solvents.



8a R = 3,4,5-trimethoxyphenyl; **8b** R = 3,4-dimethoxyphenyl;
8c R = 3,4-methylenedioxyphenyl;

But the received sodium-salts (**8a,b,c**) were not able to react with p-TOS. The sodium-salts of **5,6,7** reacted *in situ* with acylation agents and so acyl-derivatives were prepared with lower yield enough.

The demethylation of Trimethoprim by 48% Hydrogen bromid is known from the literature (U.S.P. 3,684,810). This method was applied at **5—7** but we prepared only the starting materials.

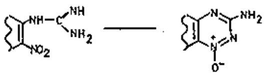
The bacteriostatic mechanisms of sulfonamido-Trimethoprim combinations were examined. (Tóth-Martinez, B. Biochem. Pharm. Vol. 26. p.p. 451—456.) Our compounds have antibacterial activity and there are pure competitive inhibitors against p-aminobenzoylglutamate and quasi-irreversible competitive inhibitors against dihydrofolatreductase.

PO 49

NEW RINGTRANSFORMATION OF AS-TRIAZINES

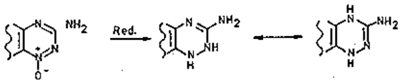
Benkó, P*., Berényi, E., Góra, L.
EGYT Pharmacochemical Works, H-1475 Budapest, PF. 100.

Some as-Triazine (**2**), condensed with N-heterocyclical ring, were synthetised by a modified method of Arndt[1,2]:



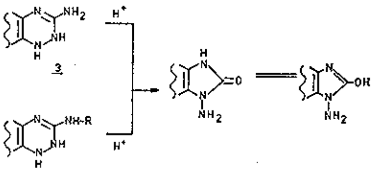
1 2

As-Triazino-(6,5-c)-chinolin and Pyrido-(4,3-e)-as-Triazine-N-oxide were reduced in the presence of sodium dithionit or catalytically and the appropriate dihydro-as-Triazines (**3**) could be isolated.



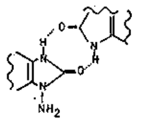
2 3

According to our experiences dihydro-derivates (**3**) has been showing activity to proton-catalytical rearrangement. Following that the transformation of **3** gave the suitable N-amino-imidazolinon (**4**), condensed with heterocyclical ring.



3 3a 4

By preparative way, it had been also proved, that the leaving group which-one nitrogenatom included. Our new compounds were identified from their analysis and spectroscopic properties (IR, NMR). IR-spectra of **4** show the next cyclic-dimer structure (**5**):



5

We studied also chemical properties of **4** be the reactions of their amino- and oxo-groups.

REFERENCES:

1) E. Berényi; P. Benkó; L. Pallos: Acta Acad. Sci. Hung. 90 (4), 395—97 (1970)

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PO 50

β-LACTAM ANTIBIOTICS WITH NOVEL RING SYSTEMS

T. E. Gunda, J. Cs. Jószberényi, E. R. Farkas
L. Kossuth University, H-4010 Debrecen, POB 33, Hungary

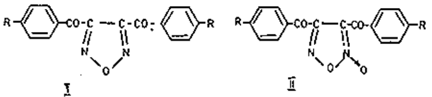
PO 51

CARBON-13 NMR INVESTIGATION OF 1,2,5-OXADIAZOLE DERIVATIVES

Halina Adamowicz, Zbigniew Buczkowski, Jerzy Lange and Hanna Tondys

Institute of Organic Chemistry and Technology, Technical University, Warsow, Poland

Carbon-13 NMR spectra of 3,4-dibenzoyl-1,2,5-oxadiazole (Ia) and its 2-oxide (IIa) as well as of the corresponding p-methyl and p-methoxy analogs were investigated in a CH_2Cl_2—$CDCl_3$ solution, chromic acetylacetonate being used in order to facilitate assignments of the quaternary carbon atoms.



I II

(a) R=H; (b) R=CH_3; (c) R=OCH_3

In the asymmetric N-oxides (II), the oxide oxygen atom produced magnetic differentiation of the corresponding carbon atoms as between the benzoyl substituents. As expected, the differences in the chemical shifts were rather small; they amounted to 1.32—1.43 ppm for the carbonyl carbon atoms, 0.82—0.94 ppm for the ortho carbon atoms, 0.20—0.22 ppm for the meta carbon atoms and 0.08—0.17 ppm for the para carbon atoms. It is noteworthy that no magnetic non-equivalence was observed for the aromatic carbon atoms in the closest vicinity of the carbonyl group. This may be considered as an indication that the differentiation observed, in particular that pertaining to the aromatic portions of the molecule, originates from the N — O bond anisotropy rather than from inductive and mesomeric effects transferred through the electron system. In each case, lower values of the chemical shifts were noted for the benzoyl moiety juxtaposed to the oxide. In IIb and IIc, the methyl group carbon atoms, sufficiently remote from the anisotropy source, proved magnetically equivalent. The effect of the N-oxide was particularly pronounced in the case of the oxadiazole carbon atoms C(3) and C(4). In Ia, for example, the two carbon atoms were equivalent with the chemical shift of 152.86 ppm. In the corresponding N-oxide (IIa), the difference in the chemical shifts was remarkably large (about 42 ppm) owing to the striking upfield shift of the C(3) signal (111.58 ppm as compared with 154.28 ppm for C(4)).

PO 52

AN INTERESTING AZIDO-TETRAZOLO TRIPLE EQUILIBRIUM; STRUCTURE ELUCIDATION OF THE ANGULAR TETRAZOLO (5,1-c) BENZO-as-TRIAZINE

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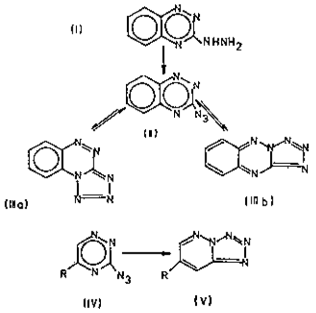
Central Research Institute for Chemistry of the Hungarian
Academy of Sciences, Budapest

It has been published[1] that the reaction of 3-hydrazino-benzo-as-triazine (I) with nitrous acid leeds to the formation of 3-azidobenzo-as-triazine (II) which results, through an equilibrium, in the angularly fused tetrazolo (5,1-c) benzo-as-triazine (IIIa). Possible formation of the angular system (IIIa) instead of the other isomer (IIIb) was supported by theoretical consideration.

Recently, W. Paudler et al.[2] criticized the angular structure of III. They found that 3-azido-as-triazine (IV) gives rise to the formation of tetrazolo(1,5-b)as-triazine (V). On the basis of this analogous system (V) they proposed the linearly fused structure (IIIb) instead of the angular (IIIa).



In order to prove the structure of the compound in question (III), ^{51}N-containing IIIa and its dihydro derivative were synthesized and investigated by MS spectroscopy.

The azido-tetrazolo equilibrium of II and III was studied by ^{13}CMR spectroscopy in detail. An interesting triple equilibrium of the azide (II) and the two tetrazoles (IIIa, IIIb) was observed. The results of the two spectroscopic methods unambigously proved, however, major participation of the angular IIIa structure both in solution and in solid phase. Theoretical consideration points rather to formation of IIIa than IIIb.

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PO 53

CYCLIZATION OF STABLE AZIDOAZOMETHINES TO TETRAZOLE DERIVATIVES

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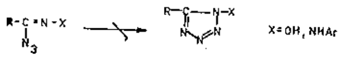
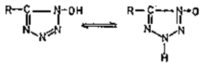
University, 00-662 Warsaw, Poland

It is known, that replacement of the halide from hydrazonyl halides[1]) and hydroxamoyl halides[2]) with azide ion yields the appropriate azides, which do not cyclize to the expected 1-hydroxytetrazoles:



As it was mentioned in the preliminary communication[3]), aromatic azidoximes can be cyclized by treatment with acyl halides. Recently I have established, that the first step of the reaction is the acylation of azidoxime, followed by protonation which causes cyclization to 1-0-acyloxytetrazole. O-Acyloxytetrazoles were next transformed into the appropriate hydroxy derivatives. The reaction was applyied to preparation of aromatic, aliphatic and heterocyclic 5-substituted-1-hydroxytetrazoles.

For these compounds the existance in two tautomeric forms according to the following equilibrium is possible:



The results of spectral and chemical investigations supports the hydroxyimine structure concept.

The action of acyl halides on hydrazonyl azides is currently investigated.

REFERENCES:

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PO 54

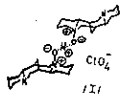
INVESTIGATION ON THE HYDROGEN BONDING IN PROTONATED QUINOLIZIDINE DERIVATIVES

Władysław Boczoń1), Maria Danuta Bratek-Wiewiórowska2),
Zygmunt Kałuski1), Jerzy Skolik3), Maciej Wiewirówski1)

(1-Institute of Chemistry, A. Mickiewicz University; 2-Institute of Organic Chemistry, Polish Academy of Sciences; 3-Department of Organic Chemistry, Academy of Economy; — Poznań — Poland)

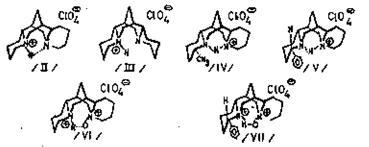
The influence of intra- and/or intermolecular factors on stereochemistry of protonated molecules of parent diamines and their mono-N-oxides in the following compounds was studied:

A. Semiperchlorate salt of sparteine-epi-N(16)-oxide (I)[1]:

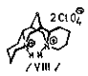


/I/

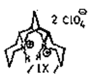
B. Monoperchlorate salts of: sparteine (II)[2], alpha-isosparteine (III)[3], 2-methylsparteine (IV), 2-phenylsparteine (V), sparteine-N(16)-oxide (VI)[4], 2-phenylsparteine-N(16)-oxide (VII)[5,6]:



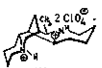
C. Diperchlorate salt of: sparteine (VIII)[3], alpha-isosparteine (IX)[3,7], 17-methylsparteine (X)[8]:



/VIII/

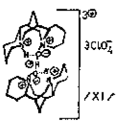


/IX/

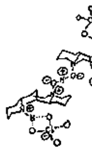


/X/

D. Sesquiperchlorate salts of: sparteine-N(16)-oxide (XI)[9], sparteine-epi-N(16)-oxide (XII)[1,10]:



/XI/



/XII/

On the basis of X-rays and complex spectroscopic data, the following problems are discussed:

— the length and the angles of the following hydrogen bonds:

$N^+ - H \cdots\cdots N$ $\quad$ $N^+ - H \cdots\cdots O^- - N^+$

$N^+ - O^- \cdots H^+ \cdots O^- - N^+$ $\quad$ $N^+ - H \cdots - OClO_3$

— the influence of geometry of intramolecular hydrogen bond on torsion angles in the quinolizidine rings and on the length of bonds:

$$N^+ - O \text{ and } N^+ - C;$$

— the influence of methyl and phenyl substituents (in 2 and 17 positions) on the pKa values of investigated compounds and on the geometry of hydrogen bonds in these compounds.

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PO 55

TRANSANNULAR NITROGEN-CARBONYL INTERACTION STUDY IN SOME QUINOLIZIDONE-2 DERIVATIVES BY THE CIRCULAR DICHROISM METHOD

W. Wysocka and J. Gawroński

Institute of Chemistry, A. Mickiewicz University, Poznań, Poland.

CD data for 13-ketosparteines and related compounds provide direct evidence for the process of protonation, involving transannular interaction of the carbonyl and amine functions in the ring D-boat form. Transannular interaction is found to occur both in 11α and in (more rigid) 11β series. In the 11α series transannular interaction in ring D requires ring C to adopt a boat conformation.

The ring D-bridged forms are evidently stabilized in water and presumably in other protic solvents. In the absence of 2-oxo function the process of transannular interaction upon acidification is retarded due to the intramolecular hydrogen bonding between N(1) and N(16).

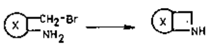
PO 56

THE AZETIDINE RING-CLOSURE REACTION OF **cis**- AND **trans**-2-(BROMOMETHYL)CYCLOALKYLAMINES

Gy. Göndös, K. L. Láng and G. Bernáth

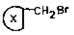
Institute of Organic Chemistry, József Attila University, Szeged, Hungary

Azetidine ring-closure reaction of cis-and trans-2-(bromomethyl) cycloalkylamines (1), involving neighbouring group participation, was investigated by kinetic and preparative methods. Comparison was made with the solvolysis processes of the corresponding (bromomethyl)cycloalkanes (3) as reference compounds.



(1) (2)

X= 5,6,7 ; cis or trans



(3)

X= 5,6,7

The first-order rate constants of the azetidine formation reactions as a function of the ring size follow the sequence cycloheptane < cyclopentane < cyclohexane for the **cis** isomers; and cycloheptane < cyclohexane for the **trans** isomers. No azetidine formation could be induced from **trans-2-(bromomethyl)cyclopentylamine**. When the Δ^{++} values of the reactions are plotted as a function of ΔS^{++} — which the exception of **trans-2-(bromomethyl)cyclohexylamine**, where the main reaction is elimination — an isokinetic correlation is manifested.

The n.m.r. spectra of the azetidines and of the 2-(bromomethyl) cycloalkylamine hydrobromides, in which the protons of the bromomethyl group are not equivalent, are discussed.

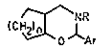
PO 57

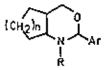
SYNTHESIS AND CONFORMATION OF STEREOISOMERIC **cis**- AND **trans**-TETRAMETHYLENE- AND PENTAMETHYLENE-DIHYDRO- AND TETRAHYDRO-1,3-OXAZINES

G. Bernáth, L. Gera, J. Kóbor*, A. Kálmán** and P. Sohár*

Institute of Organic Chemistry, József Attila University, Szeged, *Chair of Chemistry, Juhász Gyula Pedagogical Training College, Szeged, **Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, *Pharmaceutical Research Institute, Budapest

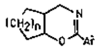
Starting from **cis**- and **trans**-2-aminomethylcyclohexanol and **cis**-**trans**-2-hydroxymethylcyclohexylamine, as well as from the homologous cycloheptane derivatives, **cis**- and **trans**-5,6-tetramethylene- and pentamethylene-5,6-dihydro- and 2,3,5,6-tetrahydro-4H-1,3-oxazines and **cis**- and **trans**-4,5-tetramethylene- and pentamethylene-4,5-dihydro- and 2,3,4,5-tetrahydro-6H-1,3-oxazines were prepared.

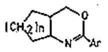




n=2,3 , cis or trans;

$R=H, CH_3, C_6H_5CH_2$





n = 2,3 ; cis or trans

The mechanism of dihydrooxazine formation with ethyl p-chlorobenzimidate is discussed. The kinetics of the quaternization reactions of N-methyl- and N-benzyl-tetrahydrooxazines were investigated. The preferred conformation of some of the above cis-fused heterocycles was determined by ^1H- and ^{13}C n.m.r. analysis and by X-ray study.

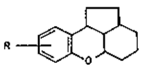
PO 58

PREPARATION OF XANTHENE DERIVATIVES BASED UPON THE REACTIONS OF ALKENYLPHENOLS

P. S. Belov, V. R. Melikyan, B. P. Tonkonogov, E. M. Lvova

The Moscow Institute of Petrochemical and Gas Industry named after I. M. Gubkin

We have studied the novel synthesis of some xanthene derivatives by the reaction of phenols with 4,7,8,9 — tetrahydroinden catalyzed by cationexchange resin „KY-2". The phenolic compounds used included phenol, ortho-, meta- and para- cresols. As a result of the reaction a number of substituted xanthenes was obtained. These compounds had the general structural formula of:



$R = CH_3$

It has been found that the addition of phenols takes place at five-membered ring double bond of 4,7,8,9 — tetrahydroinden.

The phenol addition proceeded to position 1 of 4,7,8,9 — tetrahydroinden, while six-membered ring double bond migrated from position 5 to position 6.

Phenols, treated with 4,7,8,9 — tetrahydroinden, also formed the phenolic compounds.

The obtained products were identified with the help of spectra and elementary analyses, IR- and NMR- spectra were consistent with the assigned structure.

It has been discovered that the xanthenes yield depends on position of CH_3- substituent in phenols.

PO 59

CYCLIC ACETALS BY 3,5-DI-TERT-BUTYL-4-OXYBENZALDEHYDE

M. R. Skurko, P. S. Belov

Moskow Petroleum Institute, named after I. M. Gubkin, USSR

The condensation of 3,5-di-tert-butyl-4-oxybenzaldehyde with 1,3-di- and polyoles was lead to corresponding steric hindered phenols which contain a cycloacetal group. The influence of glycols structure on director of this reaction was studied and the optimal conditions of synthesis were determined. The derivatives of pentaerytrite and 1,1,1-trioxymethylalkanes give a maximal yields in the line of obtained substances.

The correlation betwen σ_p and σ_R parametres and spectral charasteristics of steric-hindered phenols allowed quantitavly to value the influence of different substitutes in heterocyclic fragment on physical-chemical properties and steric structure of molecules.

The radical polymerization of several oleffine esters at the presence of synthesized substances has been studied and their inhibition effect has been estimated.

It was established that all of the obtained 2-(3,5-di-tertbutyl-4-oxyphenyl) -1,3-dioxacyclanes are antioxydants and value of rate constants of individual oxydation reactions were calculated.

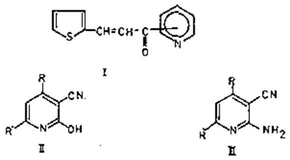
PO 60

REACTION OF 1-(X-PYRIDYL)-3-(2-THIENYL)-2-PROPEN-1-ONE WITH MALONONITRILE AND ETHYL CYANOACETATE

A. Attia*, M. Michael, S. A. Zayed

National Research Centre, Dokki, Cairo, Egypt

1-(X-pyridyl)-3-(2-thienyl)-2-propen-1-one (I) react with malononitrile and with ethylcyano acetate in presence of ammonium acetate to give rise cyanopyridines of the type II and III resp. in good yield (always axeeding 75 %).



R = 2-thienyl

R' = 2-, 3-, or 4-pyridyl

Hydrolysis and gringard reaction on the cyano group were carried out. The structure of the resulted compounds is inferred by spectral data.

PO 61

SILICON-FUNCTIONAL FURYL- AND THIENYLSILANES

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Furyllithium reacts with hydrochlorosilanes to give furylhydrosilanes. Concurrently, substitution of the Si-H bond takes place and in the case of trichlorosilane this process becomes prevailing. Organomagnesium synthesis provides considerably higher yields of 2- and 3-furylhydrosilanes and 2-thienylhydrosilanes (80—90%).

3-Furylmagnesium chloride reguired for the reaction can be obtained from 3-furyllithium and magnesium chloride.

Furyl- and thienylhydrosilanes are readily added to the double bond of 1-vinyl-2,8,9-trioxa-5-aza-1-silatricyclo(3,3,3,$0^{1,5}$)undecane to form β-isomers. The rate of hydrosilylation in the presence of platinum catalysts increases parallel to the number of heteryl groups in the molecule.

Furyl- and thienylhydrosilanes need no catalyst to undergo dehydrocondensation with amino alcohols. The reaction rate grows with the increase in the number of heteryl groups and it diminished in the following order: 2-furyl $>$ 2-thienyl $>$ phenyl. 2-Furylhydrosilanes are more reactive as compared to the appropriate 3-isomers. The rate of their dehydrocondensation with aliphatic alcohols in the presence of organic bases is augmented along with the increase in electron-accepting capacity of the substituent in the alkanol.

The use of platinum catalysts in the dehydrocondensation reaction is a suitable method for the production of trifurylalkoxysilanes. The corresponding di- and trialkoxy- derivatives of 2--(3-)furyl- and thienylsilanes were synthesized by alcoholysis of heterylchlorosilanes which were obtained by organolithium synthesis from silicon tetrachloride.

The reaction of 2-furyllithium with tetraethoxysilane results in 2- furyltriethoxysilane, whereas in the case of chloromethyltriethoxysilane the reaction proceeds both at C-Cl and Si-O bonds. Linear and cyclyc furyl- and thienyl(aminoalkoxy)silanes were obtained by means of transesterification of heterylalkoxysilanes with amino alcohols. The 3-furyl derivatives synthesized exert significantly higher toxicity than the 2-isomers.

PO 62

INVESTIGATION OF THE RELATIVE RATE OF NITRATION OF FIVE-MEMBERED HETEROAROMATIC COMPOUNDS BY' THE COMPETITION METHOD

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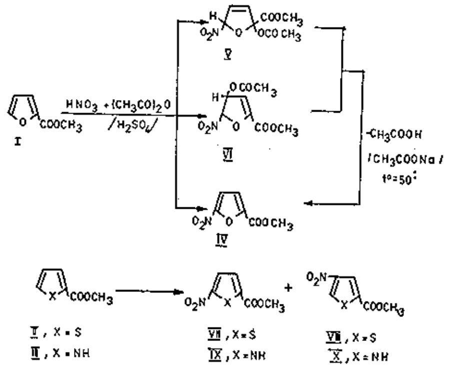
There are some complications with measurement of the reactivity of the furan compounds in the nitration reaction that are due to the low stability of furan ring under strong-acid conditions. Perhaps this is the reason why comparative data on furans and other five-membered heterocycles are not to be found in the literature.

For our investigations we selected a relative acid-resistant compound - methyl 2-furoate (I) which was compared with analogous thiophene and pyrrole derivatives (compounds II and III) in the nitration reaction using the competition method.



Nitration of compound I with acetyl nitrate (formed by the addition of nitric acid to acetic anhydride) gives methyl 5-nitro-2-furoate (IV) and adducts V and VI. The latter are treated with sodium acetate to be converted into compound IV. Analogous nitration of compound II gives a mixture of compounds VII and VIII (in ratio 1,44 : 1) but compound III gives IX and X (in ratio 3 : 1).

The relative reactivity of compounds I—III has beeninvestigated by the method of competition nitration using small quantity of nitrating agent. Ratios of the formed nitroproducts give evidence of the relative velocity of the initial attack of the carbon atoms of heterocycles by the active nitrating particle. Separation, estimation and quantitative determination of the starting materials and reaction products have been performed using TLC and GLC. The results of our investigation support such a sequence of relative reactivities of heterocycles: pyrrole 〉 furan 〉 thiophene, which is in good agreement with the results obtained in the investigation of the above heteroaromatic compounds in other electrophilic and radical reactions.

PO 63

CATALYTIC SYNTHESIS AND CONVERSION OF HETEROCYCLIC ALDEHYDES

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Aldehydes in the pyridine and diazine series have found wide application as semiproducts in the synthesis and production of medicoments, agricultural chemicals and analytical reagents.

Vapour-phase oxidation of 2-, 3-, 4-mono-, 2,3-, 2,4-, 2,5-, 2,6-di-, 2,4,6-trimethylpyridines, methylpyrazine and 4-methylpyrimidine to the corresponding formyl derivatives was studied at 250—450 °C using vanadium-molybdenum catalysts with various ratios of vanadium and molybdenum oxydes.

Selectivity of aldehydes formation was analysed as to the catalyst composition and reaction conditions. It was found that the highest yield of monopyridinaldehyles could be gained when the catalyst contained mainly the solid solution of MoO_3 in V_2O_5, whereas dialdehyde formation in the reaction of 2,6-dimethylpyridine oxidation was maximal on the vanadium-molybdenum catalysts having predominantly MoO_3 (hexagonal and rhombic forms). On the catalysts containing equal amounts of both oxides maximum yields of diazinaldehydes were obtained. Interaction between methyl derivatives of pyridines and diazines with the active centres on the catalyst surface was studied using IRS, EPR and UVS methods.

It was established that aldehydes are formed on the catalyst surface on heating the adsorbed methylazines in the oxygen. A possible mechanism explaining oxidative conversions of methylpyridines and the corresponding aldehydes on the vanadium-molybdenum catalysts is suggested on the basis of 2-methyl-, 2,6-dimethylpyridines, pyridine-2-carboxaldehyde, 6-methylpyridine-2-carboxaldehyde and pyridine-2,6-dicarboxaldehyde oxidation kinetics data. Parallelconsecutive model is suggested as the most plausible mechanism for the reaction of methylpyridines. On the other hand, oxidation of 2,6-dimethylpyridine to pyridinedicarboxaldehyde proceeds mainly in a consecutive manner via 6-methylpyridine-2-carboxaldehyde.

It is assumed that in the process of methylpyridine and pyridinecarboxaldehyde oxidation different sites of the catalyst are implicated.

The effect of H_2O vapours on the adsorption and oxidation of methylpyridines and pyridinaldehydes on vanadiummolybdenum catalysts was investigated to reveal that water promotes accumulation of pyridinaldehydes, apparently, by inhibiting their consecutive conversions.

Conditions have been worked out for the catalytic synthesis of 2-, 3-, 4-pyridine-, 3-methylpyridine-2-, 4-methylpyridine-2-, 5-methylpyridine-2-, 2-methylpyridine-4-, 6-methylpyridine-2-aldehydes and pyridine-2,6-dialdehyde pyrazinaldehyde and 4-pyrimidinaldehyde by means of vapourphase oxidation of the appropriate methyl derivatives. The present method provides production of the above compounds at the rate of 200 g/l h, with 60—80 % selectivity.

PO 64

THE INFLUENCE OF THE STRUCTURE OF OXYGEN AND NITROGEN CONTAINING HETEROCYCLES ON THEIR CHROMATOGRAPHIC BEHAVIOUR

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Gas-chromatographic behaviour of 5- and 6-membered nitrogen and oxygen containing heterocyclic compounds was studied with respect to their molecular structure. The value of retention indices I, homorphy factors H and their differences ΔI and ΔH between nonpolar (apiezon M) and polar (polyethyleneglycol 2000) stationary phases were determined for the following series of compounds: pyrrole, pyrrolidine, pyridine, piperidine, pyrazine, piperazine, triethylenediamine, morpholine, furan, furanidine, tetrahydropyran, and dioxane. Retention indices I of the above series of compounds were found to be correlated with their boil. t° and could be depicted by the linear equation $I = a(\text{boil. } t^\circ + b)$, where a and b are constant. On the diagrams representing the values of retention indices on sorbenst of various polarity, heterocyclic compounds belonging to different series, were characterized by straight lines situated in various parts of the plot, according to their affinity to specific intermolecular interaction with the stationary phases. Such interaction was best pronounced in N-unsubstituted pyrroles, followed by pyrazines and pyridines; where- as N-substituted saturated heterocyclic compounds, furan, furanidine and their derivatives interact with the sorbent in smaller extent.

The values of I, H, ΔI, and ΔH in heterocyclic systems were shown to consist of individual contributions of all structural elements, that constitute the molecule. The contributions to the values of I, H, ΔI, and ΔH of such structural elements as heteroatoms O and N, methyl and amino groups with respect to their position in the ring were measured. Thus, substitution of methylene group for an oxygen atom in the ring of cyclopentadiene at 180 °C is characterized by the value of 75 units, while in the ring of cyclopentane, cyclohexane and piperidine, by 180 units. The corresponding values for $-CH_2- \rightarrow -NH-$ substitution in the cyclopentanes, cyclohexane, piperidine, tetrahydropyran, and pentadiene rings are 255, 220, 220, 210, and 560 units, respectively. Substitution of $-CH=$ for $-N=$ in the aromatic nucleus gives the following values of ΔH increments, 195, 175, 200, 200, 170, 90, 55 in the cases of benzene, o-, m-, and p-positions in toluene, o-position in m.xylene, and m- and p-positions in pyridine, respectively.

The values of the increments measured were found to differ significantly from those obtained for the same structural elements in aliphatic and aromatic compounds. The effect of steric hindrance on the values of N atom increments in I, H, ΔI, and ΔH was noted. On the basis of the additivity of increments contributed by different structural elements a method for qualitative analysis of oxygen and nitrogen containing heterocyclic compounds without the use of standard substances has been proposed.

PO 65

PREPARATION AND SOME HETEROLYTIC REACTIONS OF CYCLIC ACETALS

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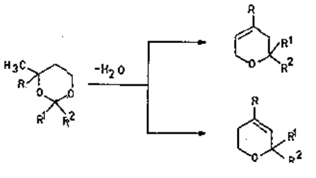
Preparation of cyclic acetals and their heteroanalogues as a result of acetalization reaction, reacetalization and exchange of aldehyde, ketones, glycols, α- and β-oxides, orthoesters, 1,3-dioxa-, oxathia- and dithiacycloalkanes was investigated. It was stated that some 1,3-dioxanes intermolecularly dehydrated into isomeric dihydropiranes under acid catalysis conditions:



R, R¹, R² = alkyl, cycloalkyl, phenyl.

The possibility of recyclization is provided by the presence of electrodonor substitutors at C_4.

Alkyl, phenoxy- and amino-derivatives were prepared by the reaction of substitution of halogen- and alkoxy-containing 1,3 dioxacyclanes.

By NMR ^1H and ^{13}C methods configuration and conformation of synthesized substances are designed.

By kinetic methods some rules of discussed reactions are stated and and they are coordinated with quantum-chemical calculations.

PO 66

SYNTHESIS AND STRUCTURE OF 1,3-OXAZOLIDENES

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3-alkyl(aryl)-1,3-oxazolidenes were synthesized by condensation of oxyethylalkyl (aryl) amines with carbonyl-containing compounds. Structure and stereochemistry of heterocyclic compounds obtained were studied by NMR on the nuclei of ^1H and ^{13}C. It was shown that formaldehyde derivatives are subjected to quick pseudorotation resulting in protons of methylene groups adjacent with a heteroatom appearing as two triplets. Complex multiplet from 4 protons in PMR-spectrum of 2 alkyl (aryl)-1,3-oxazolidenes is observed. It shows non-equivalence of all protons at C^4 and C^5 carbon atoms. The influence of electro-donor and acceptor substituters in the second position of ring on values of chemical shifts of nuclei ^{13}C in 1,3-oxazolidene-cycle and alkyl (aryl) group was studied.

Activity of 1,3-oxazolidenes in heterocyclic reactions was determined and correlation between reactivity and parameters of NMR-spectrum was found.

PO 67

INVESTIGATIONS IN THE FIELD OF CHEMISTRY AND TECHNOLOGY OF 1,3-DIHETEROCYCLANES

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Data concerning reaction mechanisms of 1,3-dioxacyclanes formation by condensation of aldehydes with olefins, acetalization and reacetalization are given.

Synthetic potentials of acid-catalyzed conversions of 1,3-dioxacyclanes under the action of alcohols, thiols, amines and esters are studied.

It has been shown that in the limiting stage the splitting of heterocycle along carbon-heteroatom bond takes place.

Phenoxy-, amino-, alkoxysubstituted 1,3-dioxacyclanes were investigated.

General rules of addition and substitution reactions in cyclic acetals are discussed. It has been stated that preparation of thermodynamically unstable stereoisomers in alkyl 1,3-dioxacyclanes series is possible when initiated by donors of free radicals addition of cyclic acetals to ethylene.

PO 68

REACTIVITY OF CYCLIC ACETALS AND THEIR HETEROANOLOGUES IN RELATON TO OXYGEN- AND CARBON-CENTERED RADICALS

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It was stated by EPR method that hydroxyl radicals abstract hydrogen atoms from cyclic acetals with cyclic di- and mono-alkoxyalkyl radicals formation. The influence of cycle size and position of alkyl substituents on radical formation selectivity is discussed.

Alkoxyl radicals abstract hydrogen atom either from methylene or methin group adjacent with two heteroatoms much more selectively than from other positions in a molecule. The influence of 1,3-diheterocyclanes structure on relative constant of velocity of hydrogen abstracting by tert-butoxyl radicals was *determined.*

As a result of investigation of liquid-phase initiated oxidation constants of velocity of reactions of peroxyl radicals with cyclic acetals were measured. It was shown that cyclic radicals are mainly formed with a single electron on hydrogen atoms being in α-position to heteroatoms.

Reactivity of 1,3 oxaheterocyclanes in relation to primary, secondary, tertiary and α,α-dichlor-alkyl radicals is estimated. Factors determining activity of cyclic acetals and their heteroanalogues in homolytic liquid phase reactions were defined.

PO 69

AN INVESTIGATION OF FURFURAL NITRATION IN ACETIC ANHYDRIDE

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