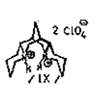
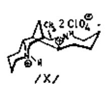
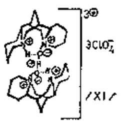
C. Diperchlorate salt of: sparteine (VIII)[3], alpha-isosparteine (IX)[3,7], 17-methylsparteine (X)[8]:

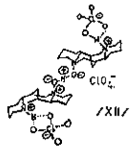

/VIII/


/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:

$N^+ — H . . . . . N$ $N^+ — H . . . . . O^- — N^+$

$N^+ — O^- . . . H^+ . . . O^- — N^+$ $N^+ — H . . . —OClO_3$

— 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

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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

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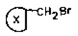
Azetidine ring-closure reaction of cis-and trans-2-(bromomethyl) cycloalkylamines (1), involving neighbouring group participation, was investigated by kinetic and preparative methods. Comparison was made with the solvolysis processes of the corresponding (bromomethyl)cycloalkanes (3) as reference compounds.

(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

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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

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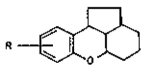
The Moscow Institute of Petrochemical and Gas Industry named after I. M. Gubkin

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

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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 stodied and the optimol 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

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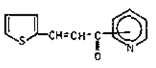
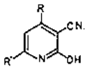
National Research Centre, Dokki, Cairo, Egypt

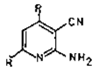
1-(X-pyridyl)-3-(2-thienyl)-2-propen-1-one (I) react with malononitrile and with ethylcyano acetate in presence of ammonium acetate to give rise cyanopyridines of the type II and III resp. in good yield (always axeeding 75 %).



I



II



II

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.