LE I 1

SYNTHESIS OF NEWER XANTHOTOXIN-4-SULFONAMIDES AND XANTHOTOXIN-4-SULFONIC ACID ESTERS WITH POTENTIAL ANTIMICROBIAL EFFECT

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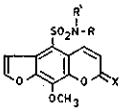
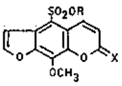
Xanthotoxin-4-sulfonyl chloride reacts with an appropriate amino derivative or phenol to give the corresponding xanthotoxin-4-sulfonamides (I) or xanthotoxin-4-sulfonic acid esters (II) respectivly. The structural assignments of the obtained products are based on analytical, chemical and spectroscopic results. Sulfonamides (I) have been subjected to the action of s-benzylisothioronium hydrochloride, and reacted with dimethyl sulfate yielding the methylated sulfonamides with no cleavage of the coumarin ring. Thionation of the synthesised products by the action of P_2S_5 afforded the corresponding thioxanthotoxin derivatives in good yield.

IR and UV data is discussed. The quite promising results of the antimicrobial activity of the resulted compounds is presented.



(I)



(II)

X = O or S.

LE I 2

SYNTHESIS AND PROPERTIES OF OXODIHYDROFURANS

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LE I 3

OXYGEN-CONTAINING HETEROCYCLES ON THE BASIS OF 1,3-DIOLS. SYNTHESIS AND PROPERTIES

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LE I 4

1,3-DIOXOLANIUM SALTS AND THEIR APPLICATION IN ORGANIC CHEMISTRY

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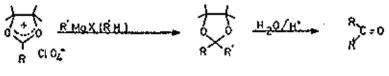
A simple synthetic route to 1,3-dioxolanium salts, wich consist of acylation of pinaconic glycols by anhydrides and acyl chlorides in the presence of perchloric acid or $AgClO_4$ has been developed.

R = Alk, Ar, CH_2Ar

The salt of 1,3-dioxolanium may be used as effective alkylation and formylation agents.

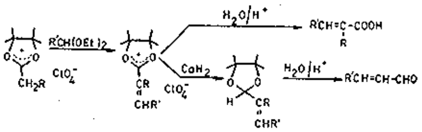
The reaction of dioxolanium salts with active aromatic, heterocyclic and organomagnium compounds lead to the formation of 1,3-dioxolanes, which by hydrolysis yields the corresponding carbonyl compounds: alkylarylketones, alkylbenzylketones, benzophenones, deoxybenzoines, aromatic, heterocyclic and arylacetic aldehydes:



R = H, Alk, Ar

R' = Alk, Ar, CH_2Ar

2-Alkylgroups of 1,3-dioxolanium salts were found to be active in the reactions of condensation with acetals of aromatic and heterocyclic aldehydes and orthoesters.



R = H, Alk, Ar

R' = Ar, Het., OEt

Hydrolysis or reduction of 2-styryldioxolanium salts lead to α,β-unsaturated acids and cinnamic aldehydes, respectively.

This method allows to prolong the carbon chain of carbonyl compounds.

The reactions of 2-β-ethoxyvinylsubstituted 1,3-dioxolanium salts with wather, amines or organomagnium compounds has been discussed.

Cyanine dyes have been prepared based on the 1,3-dioxolanium salts and its derivotives.

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LE I 5

NEW POSSIBILITIES OF APPLICATION OF FURFURAL FOR THE SYNTHESES OF SELF-EXTINGUISHING POLYURETHANE INTERMEDIATES

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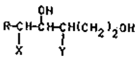
Hitherto unknown in the literature variants of converting of furfural to ethyl esters of 3-ketocarboxylic acids have been elaborated and the attempts of reduction of the latter compounds into appropriate glycols have been conducted. The general aim of the undertaken investigations was to obtain diols, that together with organic diisocyanates give the resistant to temperature, slow burning and self-extinguishing polyurethane resins. As the result, of 'undertaken in this field experimental studies the compounds I—IV of the general formula „A" given below, have been obtained.



$$\underset{X}{R-CH}-\overset{OH}{CH}-\underset{Y}{CH}(CH_2)_2OH$$

"A"

Hexanediol-1,4 (I); (A, when R = CH_3, X = Y = H
5-Bromohexanediol-1,4 (II); (A, when R = CH_3, X = Br, Y = H)
3,5-Dibromohexanediol-1,4 (III); (A, when R = CH_3, X=Y=Br)
Heptanediol-1,4 (IV); (A, when R = C_2H_5, X = Y = H)
3,5-Dichloroheptanediol-1,4 (V); (A, when R = C_2H_5, X=Y=Cl)
3,5-Dibromoheptanediol-1,4 (VI); (A, when R=C_2H_5, X=Y=Br)

The first stage of syntheses of the above mentioned glycols I—IV consisted in treating furfural with methylmagnesium iodide or ethylmagnesium bromide. As the result of this reaction, the appropriate alkyl(2-furyl)carbinols were formed. These alcohols subjected to the action of mineral acid in ethanol were transformed into ethyl ester of 3-ketopentanecarboxylic-1 acid, or ethyl ester of 3-ketohexanecarboxylic-1 acid. The first of these compounds, under the effect of reducing agents, gave hexanediol-1,4 (I), whereas the second ones — heptanediol-1,4 (IV). Under the effect of bromine or chloride both the esters gave the appropriate halogen derivatives, which as the result of the reduction were transformed into halogen diols II, III, V or VI. On the base of diols I/VI and tolylene-2,4-diisocyanate(2,4-TDI) or the mixture of 2,4-TDI and 2,6-TDI at weight ratio 4 : 1, not reported in literature polyurethane resins were obtained and subjected to the total derivatographic analysis. First of all thermal resistance of resins obtained from diols I and IV and appropriate TDI isomers was examined and compared with thermostability of polyurethanes obtained on the base of diols II, III, V and VI and the same diisocyanates.

The obtained results showed that resins, for the synthesis of which glycols II, III, V and VI were used, have higher thermal resistance than resins obtained on the base of diols I and II. Moreover the resins of the first type revealed the advantageous features of self-extinguishing.

On the base of the carried out investigations it has been established that halogen diols II, III, V and VI may find their application for the synthesis of self-extinguishing and slow-burning polyurethane materials.

LE I 6

SOME STRUCTURAL PECULIARITIES AND PROPERTIES OF ALUMINIUM HALIDE COMPLEXES WITH CARBONYL COMPOUNDS OF BENZENE, THIOPHENE, AND FURAN SERIES

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LE I 7

REACTIONS OF PHENYLCYCLOPROPANE WITH TETRAHALIDES OF SELENIUM

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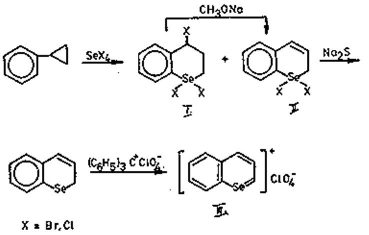
The reaction of phenylcyclopropane with the tetrahalides of selenium was investigated. It appeared that the 1,1,4-trihalogen derivatives of 1-selenochromane (I) and 1,1-dihalogen derivatives of 1-selenochrom-3-ene (II) could be obtained by heating an etheric solution of the above substances. It means that the cyclopropane ring splits and subsequently a cyclization takes place to give the benzene ring



Scheme 1

The structure of the compounds thus obtained was proved by n.m.r. spectra and by conversion of the 1,1-dihalogen 1-selenochrom-3-ene in the 1-selenochromylium perchlorate (III) described in literature (scheme 1).

The antimicrobial activity of the 1,1,4-trihalogen derivatives of 1-selenochromane and 1,1-dihalogen derivatives of 1-selenochrom-3-ene was investigated. It was revealed that these compounds exhibit antibacterial and anti-yeast activity.

LE I 8

SUBSTITUENT EFFECTS ON THE DISPOSITION OF THIIRANE 1,1-DIOXIDES AND THIIRENE 1,1-DIOXIDES IN KOH-t-BuOH.

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Treatment of sulfones with KOH-CCl_4-t-BuOH provides thiirane 1,1-dioxide and thiirene 1,1-dioxide intermediates which decompose rapidly and specifically into products whose nature is dependent on the substitution pattern of these intermediates. Some examples are: