PO 5

SYNTHESES IN THE FURAN SERIES

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PO 6

STUDIES IN PYRROLE SERIES

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The investigation of anodic behaviour of pyrroles bears a specific feature of this type of heterocycle. In contrary to furans and thiophenes a four-electron oxidation takes place in case of 1-methylpyrrole leading to 5,5-dimethoxy-1-methyl-pyrrolin-2-on as the main product.

The oxidation has been carried out in a two- or three-electrode system using platinum anode in methanolic solutions of kalium hydroxide or tetramethylammonium perchlorate.

Under similar conditions the electrochemical oxidation of some pyrrole derivatives has been studied. Thus, 1,2,4-trimethylpyrrole and 1,2,5-trimethylpyrrole, respectively, afforded products of oxidation attack on C-methyl groups, i.e. the corresponding methoxymethyl derivatives. Without obligation to protect the nitrogen atom an analogous course of reaction has been observed in case of diethyl 3,5-dimethyl-2,4-pyrrole dicarboxylic acid.

Using ammonium bromide as electrolyte a mixture of products hes been observed in oxidation of 1-methylindole among them 3,3-dibromo-1-methyl-2-indalinon, 3,3,5-tribromo-1-methyl-2-indolinon and 5-bromoisatin have been identified.

The reaction mechanism is discussed.

PO 7

MIXED HYDRIDE HYDROGENOLYSIS OF AROMATIC ALIPHATIC ACETALS. THE REACTION CONTROLLING STEP

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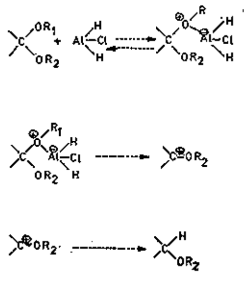
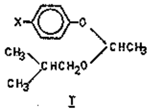
Generally, mixed hydride hydrogenolysis of acetals is supposed to proceed via the following steps:

1) formation of a complex between the acetal and the hydride,
2) formation of a stable oxycarbenium ion,
3) rapid hydride ion transfer to the oxycarbenium ion

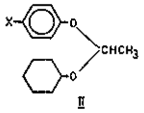


With R_1 and R_2 = alkyl, the reaction controlling step (RCS) is supposed to be the step 2). However, there have been discussions corcerning the RCS in cases where R_1 or R_2 = aryl, and step 1) has been repeatedly suggested as the RCS.

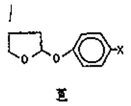
We have tried to clarify this situation by preparing mixed aromatic aliphatic acetals of the types (I), (II), (III), and (IV), measuring their k_{rel} in the reaction with chloroalane, and using the data obtained in LFER correlations (which should give reaction constants ϱ with opposite sings for RCS being 1) and RCS being 2)).



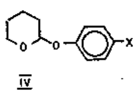
I



II



III



IV

where for all I—IV, X = H, CH_3, OCH_3, Cl, and tert-C_4H_9

The acetals I, II, III, and IV were prepare! from iso-butyl vinyl ether, cyclohexyl vinyl ether 2,3-dihydrofuran, 2,3-dihydropyran, and the corresponding p-substituted phenols, respectively. The relative rate constants k_{rel} were measured using both HPLC and ^{1}H NMR.

The correlations obtained were all satisfactory and gave positive ϱs for reactions of acetals I, II, and III, and a negative ϱ for the reaction of IV. The obtaine ϱs differ considerably in their absolute values, too.

The significance of both differencies is discussed.

PO 8

CYCLISATION OF 2-NITROARYLHYDRAZO COMPOUNDS TO 2-PHENYLBENZOTRIAZOLE-1-OXIDES

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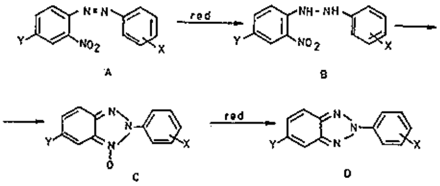
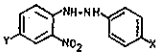
The aim of our study was elucidation of the pathway by which 2-nitroazocompounds are reductively converted into the corresponding 2-phenylbenzotriazoles.

We have shown earlier[1] that 2-nitrohydrazocompounds and 2-phenylbenzotriazole-1-oxides are intermediates in this reaction (see Scheme I).



Scheme 1

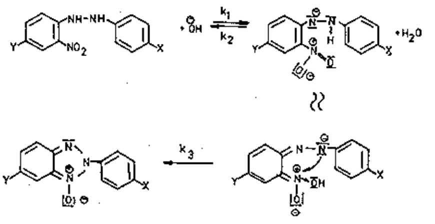
In the present paper, we will deal with our results concerning that step of the reaction in which 2-nitrohydrazo compounds (B) are converted into 2-phenylbenzotriazole-1-oxide (C).
As given in Scheme II, a series of 2-nitrohydrazobenzene derivatives was prepared.



X	Y
OCH_3	NO_2
CH_3	NO_2
H	NO_2
Cl	NO_2
CN	NO_2
NO_2	NO_2
H	H

Scheme II

Cyclization thereof gave the corresponding 2-(4-X-phenyl)-6-Y-benzotriazole-1-oxides, respectively.
Hydrazocompounds were prepared by reacting 2-nitrofluorobenzene with the corresponding 4-X-phenylhydrazine, which, in turn, were prepared by $SnCl_2$ or Na_2SO_3 reduction of 4-X-benzene diazonium salts.
The cyclisation reaction was followed spectrophotometricaly in 40% aqueous propanol by measuring the intensity of an absorption band around 300 nm corresponding to benzotriazole oxide. The effect of pH and substitution was investigated.
The kinetic measurements showed the reaction to be 1 st order in hydrazocompound (at constant pH in the region of 5,5—10,5) and the reaction rate to be pH dependent. Rate constants for cyclisation of hydrazocompounds are linearly pH dependent (the pH dependence of log k has a slope equal to 1).
Obviously, the reactions rate depends on concentration of the hydrazocompound, on concentration of hydroxide ions, and on the substituent. A mechanism of the cyclisation suggested on the basis of the above data is also in agreement with some quantum mechanical calculations.



Scheme III

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PO 9

SYNTHESES AND REACTIONS OF 2-AMINO-3-CYANO-4,5-BIS (HETARYL) FURANS AND 4-R-5,6-BIS(HETARYL) FUROPYRIMIDINES

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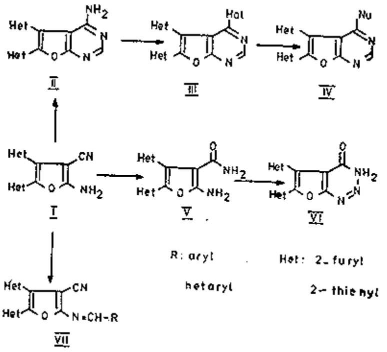
2-Amino-3-cyanofuran derivatives are not only interesting in aspect of their preparation but as the possibility of their use in another syntheses as well[1-3].
In this report, 2-amino-3-cyano-4,5-bis(2-furyl)furan Ia and 2-amino-3-cyano-4,5-bis(2-thienyl)furan Ib have been obtained by reaction from the corresponding acyloines and malononitrile. These derivatives have been utilized in another synthesis for the preparation of the furopyrimidines II—IV, furo-1,2,3-triazinones VI and Schiff's bases VII as shown the following chart[4]:



The structures of the synthesized compounds were determined by means of their IR, UV, ^1H-NMR and mass spectra. Spectral data of 2-furyl- and 2-thienyl derivatives have been compared with each other. The biological activity of some compounds mentioned above has been studied also.

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PO 10

MANNICH BASES OF 2-MERCAPTOBENZOTHIAZOLE AND THEIRS ANTIMYCOBACTERIAL AND ANTIVIRAL ACTIVITY

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The present data on the Mannich reaction of 2-mercaptobenzothiazole (2-MBT) with primary amines do not offer a satisfactory explanation, why with some amines monoderivatives and with the others bisderivatives are obtained[1].