

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 potassium 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 has 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-bromoindatin have been identified.

The reaction mechanism is discussed.

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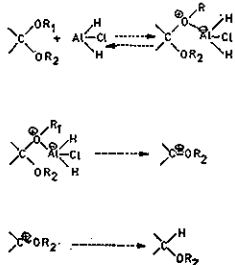
MIXED HYDRIDE HYDROGENOLYSIS OF AROMATIC ALIPHATIC ACETALS. THE REACTION CONTROLLING STEP

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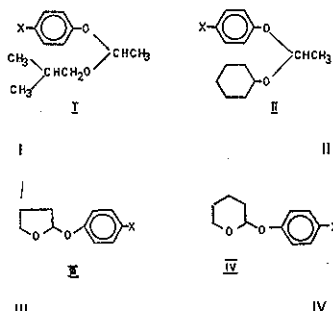
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Generally, mixed hydride hydrogenolysis of acetals is supposed to proceed via the following steps:

- 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 concerning 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 signs for RCS being 1) and RCS being 2)).



where for all I-IV, X = H, CH₃, OCH₃, Cl, and *tert*-C₄H₉. The acetals I, II, III, and IV were prepared 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 ¹H NMR.

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

The significance of both differences is discussed.

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

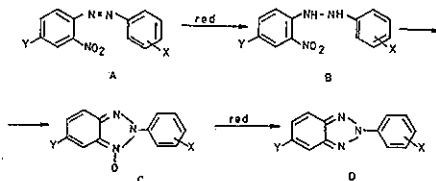
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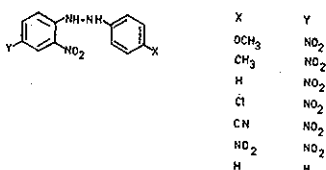
The aim of our study was elucidation of the pathway by which 2-nitroazocompounds are reductively converted into the corresponding 2-phenylbenzotriazoles.

We have shown earlier¹ that 2-nitrohydrazocompounds and 2-phenylbenzotriazole-1-oxides are intermediates in this reaction (see Scheme 1).



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.



Scheme II

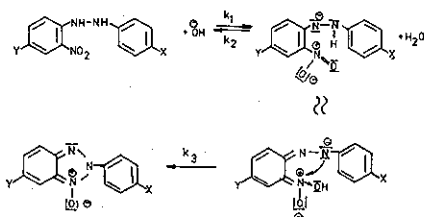
Cyclization thereof gave the corresponding 2-(4-X-phenyl)-6-Y-benzotriazole-1-oxides, respectively.

Hydrazo compounds were prepared by reacting 2-nitrofluorobenzene with the corresponding 4-X-phenylhydrazine, which, in turn, were prepared by SnCl₂ or Na₂SO₃ reduction of 4-X-benzene diazonium salts.

The cyclization reaction was followed spectrophotometrically 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 1st order in hydrazo compound (at constant pH in the region of 5.5–10.5) and the reaction rate to be pH dependent. Rate constants for cyclization of hydrazo compounds 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 hydrazo compound, on concentration of hydroxide ions, and on the substituent. A mechanism of the cyclization suggested on the basis of the above data is also in agreement with some quantum mechanical calculations.



Scheme III

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- 2) POTÁČEK M., PICKA K.: Chem. Zvesti 30, 568 (1976).

PO 9

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

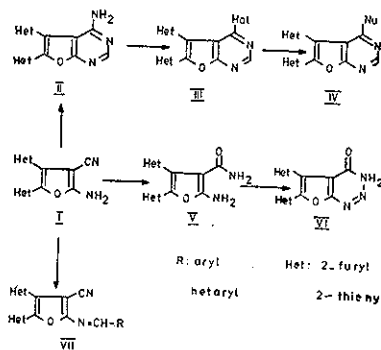
FUOPYRIMIDINES

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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 well¹⁻³.

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 acylones and malononitrile. These derivatives have been utilized in another synthesis for the preparation of the furapyrimidines II–IV, furo-1,2,3-triazines VI and Schiff's bases VII as shown the following chart⁴:



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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- 1) Gewald K.: Chem. Ber. 99, 1002 (1966).
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PO 10

MANNICH BASES OF 2-MERCAPTOBENZOTHAZOLE 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 obtained¹.