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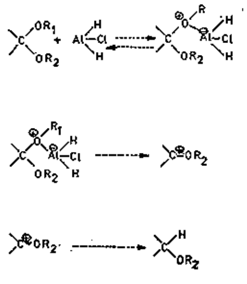
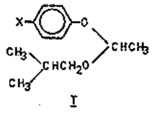
Generally, mixed hydride hydrogenolysis of acetals is supposed to proceed via the following steps:

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

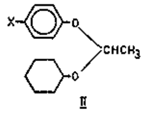


With R_1 and R_2 = alkyl, the reaction controlling step (RCS) is supposed to be the step 2). However, there have been discussions corcerning the RCS in cases where R_1 or R_2 = aryl, and step 1) has been repeatedly suggested as the RCS.

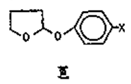
We have tried to clarify this situation by preparing mixed aromatic aliphatic acetals of the types (I), (II), (III), and (IV), measuring their k_{rel} in the reaction with chloroalane, and using the data obtained in LFER correlations (which should give reaction constants ϱ with opposite sings for RCS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



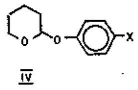
I



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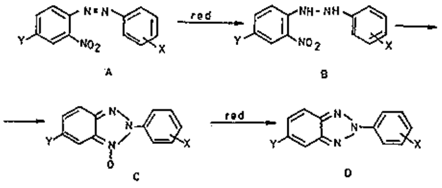
The aim of our study was elucidation of the pathway by which 2-nitroazocompounds are reductively converted into the corresponding 2-phenylbenzotriazoles.

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



Scheme 1