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THE SYNTHESES OF SOME HETEROCYCLIC COMPOUNDS FROM FURANS USING ELECTROCHEMICAL AS WELL AS PHOTOCHEMICAL TECHNIQUES

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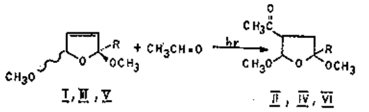
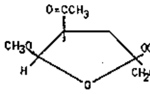
The syntheses of heterocyclic systems from 2,5-dialkoxy-2,5-dihydrofurans are well documented in chemical literature¹). Claxuson-Kaas reaction (chemical or electrochemical) of furans furnishes the wide range of the above mentioned products in excellent yields.

Unfortunately, the reactivity of the double bond of the system in question is very limited with respects to addition. Consequently, the recent synthetic research is directed mainly to the study of suitable addition reaction giving at least reasonable yields. Previously²) we have described the photochemically induced addition of acetaldehyde to 2,5-dimethoxy-2,5-dihydrofurane (I) giving 3-acetyl-2,5-dimethoxytetrahydrofurane (II) in 95% yield. It is the very aim of this contribution to deal with the scope and stereochemical aspects of this reaction.
That's why we have studied the addition of acetaldehyde to 2(RS)5(RS) 2-hydroxymethyl-2,5-dimethoxy-2,5-dihydrofurane (III), the configuration of which has been recently confirmed using X-ray diffraction method. The only product of this reaction was 2(RS)4(SR)5(RS) 4-acetyl-2-hydroxymethyl-2,5-dimethoxytetrahydrofurane (IV).

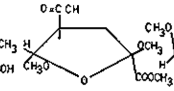


I, II R = H; III, IV R = CH_2OH; V, VI R = $COOCH_3$

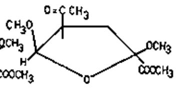
Using model compound IV we have able to resolve the configuration of methyl 4-acetyl-2,5-dimethoxytetrahydrofuran-2-carboxylate (VI). The compound VI has been obtained in two diastereoisomeric forms VIa and VIb from the photochemically initiated addition of acetaldehyde to cis, trans methyl 2,5-dimethoxy-2,5-dihydrofuran-2-carboxylate (V).



IV



VIa



VIb

The structures of IV, VIa and VIb were esteblished on the basis of elementar analysis, IR and NMR spectra, the relative ratio VIa : VIb was found 3 : 1 (NMR). All additions were carried out under nitrogen atmosphere at 10—15 °C using excess of acetaldehyde and 125W high pressure mercury lamp.

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1) ELMING N.: Advances Organic Chemistry, Vol. 2, p. 67, Interscience, New York, 1960.

2) ŠROGL J., LIŠKA F., STIBOR I., BEČKOVÁ M.: Z. Chem. *13*, 290 (1973).

LE I 10

CYCLISATION REACTION OF MERCAPTO- AND AMINO-HETEROCYCLIC COMPOUNDS WITH ARYL CYANATES AS CN-BUILDING BLOCKS

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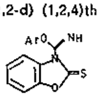
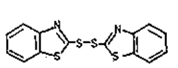
As 2-mercapto-ozoles are ambident nucleophilic compounds, they can be attacked by aryl cyanates at the exocyclic mercapto group or at the cyclic nitrogen atom. Taking 2-mercapto-benzazoles as an example we found

1. N-acylation in the case of 2-mercapto-benzoxazole with formation of the isoureas 1
2. S-acylation in the case of 2-mercapto-benzthiazole followed by the formation of bis-benzthiazolyl-disulfide 2
3. N- and S-acylation in the case of 2-mercapto-benzimidazole followed by the cyclisation to 3-aroxy-benzimidazolo (1,2-d) (1,2,4)thiadiazoline 4

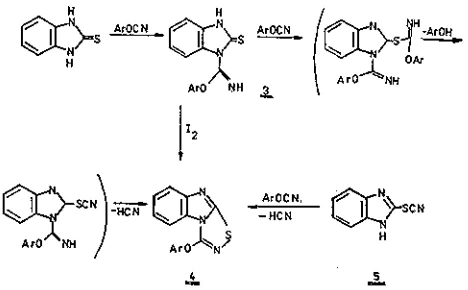


1

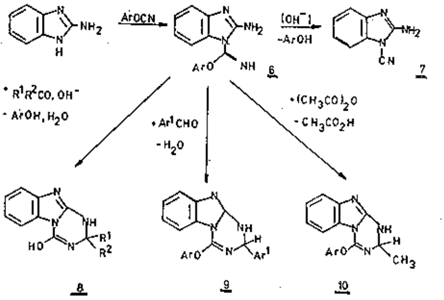


2

The mechanism of the formation of 4 is demonstrated by the independent synthesis from 2-thiocyanoto-benzimidazole 5 with aryl cyanates and by oxidation of the isourea 3 with iodine.



The application of the reactions (1) — (3) to other mercapto-N-heterocyclic compounds is also discussed.
The reaction of 2-amino-benzimidazole with aryl cyanates yields the isourea 6. The exocyclic amino group is not acylated, because the isoureas 6 form the nitriles 7 by elimination of phenoles. In the presence of molar amounts of sodium hydroxide cyclocondensation of the isoureas with carbonyl compounds with elimination of phenole takes place, and 4-hydroxy-1,2-dihydro-1,3,5-triazino(1,2-a) benzimidazoles 8 are formed. The reaction of 6 and aromatic aldehydes gives the known 4-aroxy-2-aryl-1,2-dihydro-1,3,5-triazino(1,2-a)benzimidazoles 9. With an excess of acetic anhydride the corresponding 4-aroxy-2-methyl-1,3,5-triazino(1,2-a) benzimidazoles 10 are formed.



The UV-, ¹H-NMR- and ¹³C-NMR-spectra are in accordance with the given structures.