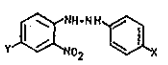
In the present paper, we will deal with our results concerning that step of the reaction in which 2-nitrohydrazo compounds (B) are converted into 2-phenylbenzotriazole-1-oxide (C).
As given in Scheme II, a series of 2-nitrohydrazobenzene derivatives was prepared.



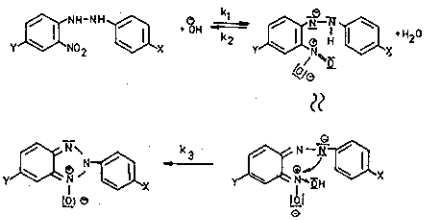
X	Y
OCH_3	NO_2
CH_3	NO_2
H	NO_2
Cl	NO_2
CN	NO_2
NO_2	NO_2
H	H

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 ón 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

REFERENCES

1) BELUSA J., KRCHŇAK V., POTÁČEK M., RABUSIC E.: Chem. Zvesti 26, 53 (1972).
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) FUROPYRIMIDINES

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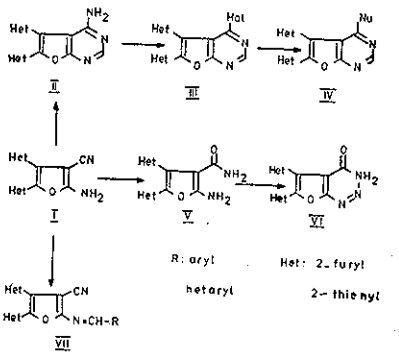
2-Amino-3-cyanofuran derivatives are not only interesting in aspect of their preparation but as the possibility of their use in another syntheses as well[1—3].

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, ^{1}H-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.

REFERENCES

1) Gewald K.: Chem. Ber. 99, 1002 (1966).
2) Sharanin J. A., Karovan V. S., Temnikova T. I.: Zh. Org. Khim. 3(11), 1987 (1967).
3) Taylor E. C., McKillop A.: The Chemistry of Cyclic Enaminonitriles and o-Aminonitriles, in Advances in Organic Chemistry: Methods and Results E. C. Taylor, Ed., Interscience Publishers, Wiley and Sons (1970).
4) Prousek J., Jurášek A., Kováč J.: Coll. Czech. Chem. Commun. - in press.

PO 10

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

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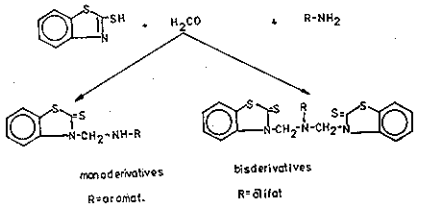
The present data on the Mannich reaction of 2-mercaptobenzothiazole (2-MBT) with primary amines do not offer a satisfactory explanation, why with some amines monoderivatives and with the others bisderivatives are obtained[1].



We have found that the amines with pK_B around 3—5 afford only bisderivatives, while those with pK_B around 9—14 gave exclusively monoderivatives[2,3]. In further series experiments we employed as aminocomponents hydrazides of aliphatic and aromatic acids. At both types of hydrazides we obtain only bisderivatives of Mannich bases.

Several of the prepared compounds showed remarkable antimycobacterial activity mainly against Mycobacterium tuberculosis resistant on the isonicotinylhydrazide[4,5].

A number of these derivatives was studied also for antiviral activity. The antiviral tests were carried out in cell cultures using vaccinia, Newcastle disease and western equine encephalomyelitis viruses. Several of derivatives tested have shown middle or slight degree of inhibition of virus multiplication.

REFERENCES

1) Stavrovskaja V. I., Kolosova M. O., Ž. Obšč. Chim., 30, 689 (1960).
2) Holbová E., Sutoris V., Blöckinger G., Chem. Zvesti, 30, 195 (1976).
3) Holbová E., Sidóová E., Odlerová Z., Chem. Zvesti, 30, 709 (1976)
4) Holbová E., Odlerová Z., AC 180893 (1975) Czechoslovakia.
5) Odlerová Z., Holbová E., IV. Congressus Pneumol. Phtiseol. International, Bratislava, Czechoslovakia, May 1976.

PO 11

A NEW METHOD OF PREPARATION OF DERIVATIVES OF PARTIALLY HYDROGENATED DIBENZO[c,h][1,2,6,7]TETRAZECINE AND ITS ANALOGUE

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5,6,7,12,13,14-Hexohydrodibenzo [c,h] [1,2,6,7]tetrazecine-7,14--dione and 5,6,7,12,13,14-hexahydrodipyrido[3,4-c,h][1,2,6,7]tetrazecine-5,12-dione were prepared by heating the hydrazide of salicylic and 3-hydroxyisonicotinic acid, respectively. Their structure was verified by elementary analysis, infra-red and mass spectra.

PO 12

CONCERTED AND STEPWISE CYCLOADDITIONS OF 1-BENZYL -4-N-ACYLIMINO-1,2,4-TRIAZOL WITH ISOTHIOCYANATES

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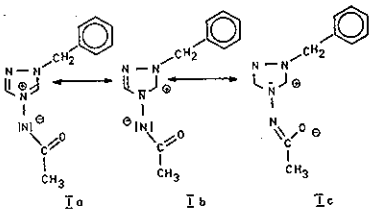
In contrast to numerous 1,3-dipolar cycloadditions, following a concerted reaction mechanism, there are few 1,5-intermolecular cycloadditions known. Since the extension of 1,3-dipol with one conjugated double bond transforms them to 1,5-dipols, theoretically there can be as much as 98 1,5-dipols.

In our case the azomethinimine system has been extended on the nitrogen end with a carbonyl group. The charge separation and its dissipation of such a dipol predisposes the molecula of 1-benzyl-4-N-acylimino-1,2,4-triazol I to both 1,3-concerted and 1,5-stepwise reaction manners.



We have investigated the possible role of nonpolar and aprotic polar solvents on the stabilisation of mesomeric forms Ib and Ic and on alternative transition states. Using benzene as solvent, I adds to aromatic isothiocyanates in 1,3-concerted manner to give stable aduct on C S bond and unstable aduct on C N bond, together with other compounds, arising either from still another mechanism, or as splitting products of unstable C N aduct of I. Polar aprotic solvents, like DMF, DMSO or HMPT favour 1,5-dipolar structure, as they bring more solvation stabilisation needed for enhanced charge separation. Concerted [6_s 2_s] reaction being disallowed, the cyclic aduct IV arises by stepwise addition. In the first step anionic terminus of 1,5-dipol atacks the carbon atom of isothiocyanate, giving noncyclic intermediate. This could be isolated and consequently cyclises to IV.

PO 13

5-NITRO-2-FURYLVINYLATION OF PHOSPHOROUS COMPOUNDS

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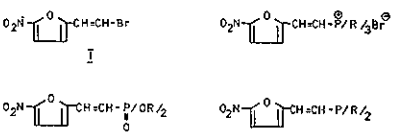
The synthesis of 5-nitro-2-furylvinylenbromide (I) which contains a sufficiently reactive bromine has opened the path for a new synthesis of biologically high active 5-nitro-2-furylethylene derivatives.

We studied a 5-nitro-2-furylvinylation of the tertiary phosphines (e.g. triphenylphosphine), tertiary phosphites (e.g. triethylphosphite) and alkali metal diphenylphosphides in the nonpolar media.



We have found that the presence of a phosphorous group on vinylene group of the nitrofurane derivative effects significantly its biological properties.