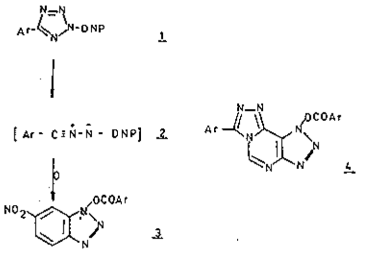
LE I 11

RING TRANSFORMATION OF TETRAZOLES INTO BENZOTRIAZOLES

E. Lippmann* and A. Könnecke
Sektion Chemie der Karl-Marx-Universität, DDR-701 Leipzig, Liebigstrasse 18

5-Aryl-2-(2,4-dinitrophenyl = DNP)tetrazoles **1** have been prepared in excellent yields by treating the appropriate 5-aryltetrazoles with 1-fluoro-2,4-dinitrobenzene in acetone/NEt_3 at room temperature.

Due to the electron attracting DNP substituent compounds **1** are thermally much more labile than other 2,5-diaryltetrazoles. They decompose cleanly with nitrogen evolution on heating in boiling benzene yielding nitrilimine intermediates **2**. Attempted 1,3-dipolar cycloadditions of **2** and dimethyl acetylenedicarboxylate or diethyl maleate failed. A faster intramolecular stabilization reaction leads to 1-aroyloxy-6-nitrobenzotriazoles **3** as the final products in yields over 93%. Thermolysis of **1** at higher temperatures did not alter this reaction pathway and in no case products arising from nitrilimine fragmentation, ArCN and 5(6)-nitrobenzofuroxan, formed **via** either intramolecular 1,3-dipolar cycloaddition or anchimeric assisted loss of ArCN, have been found.



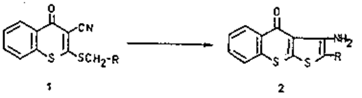
The mechanism of this transformation, involving inital 1,7-dipolar electrocyclic ring closure, will be discussed. As an example for the use of the reaction in heterocyclic synthesis the ready formation of condensed 8-azapurines **4** from 4,6-dichloro-5-nitropyrimidine will be described. Some of the tetrazoles **1** are explosives.

LE I 12

SYNTHESIS OF HETEROCYCLES WITH O-CHLORBENZOYL ACETONITRILE

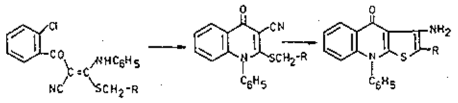
W.-D. Rudorf* and M. Augustin
Department of Chemistry, Martin-Luther-University,
DDR-402 Halle/Saale, German Democratic Republic

Reaction of o-chlorbenzoyl acetonitrile with carbon disulfide occured in the presence of sodium hydride and following alkylation to give 1-thiochromones **1**. A mechanism for the cyclisation is discussed. The compounds 1 are suitable substances for the synthesis of thieno[2.3-b]1-thiochromones **2** by nitrile cyclisation.



1 2

o-Chlorbenzoyl acetonitrile reacts with phenyl isothiocyanate/sodium hydride to the ketene S,N-acetal **3**, while the awaited 2-anilino-1-thiochromone is not obtained. Cyclisation of **3** in a basic medium forms the 4(1H)-quinolones **4**. The following cyclisation supplies 4,9-dihydrothieno[2.3-b]quinoline-4-ones **5**.



3 4 5

LE I 13

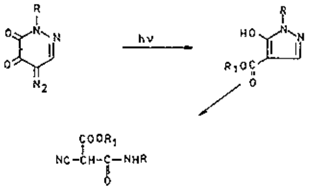
PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF SOME HETEROCYCLIC DIAZOKETONS

Branko Stanovnik* and Miha Tišler
Department of Chemistry, University of Ljubljana, Ljubljana, Jugoslavia

Heterocyclic diazo compounds are important synthons for the preparation of different heterocyclic systems and in azatransfer reactions.

Heterocyclic diazo ketones could be transformed photochemically into derivatives of ring contracted carboxylic acids. Recently, 3-diazo-4-oxo-3,4-dihydroquinoline has been converted when irradiated either into esters or amides of indole-3-carboxylic acids.

In this communication we wish to report on the photochemical and thermal transformations of 6-substituted-7-diazo-8-oxo-s-triazolo(4,3-b)pyridazines into alkyl-6-substituted-pyrazolo(3,2-c)-s-triazolo-7-carboxylates and 1-substituted-4-diazo-5,6-dioxo-1,4,5,6-tetrahydropyridazine into alkyl 1-substituted-6-hydroxy-pyrazolo-4-carboxylates and carbalkoxy substituted cyanoacettes.



Some other thermal and photochemical transformations will be discussed.

LE I 14

NEW SYNTHETIC METHODS OF HETEROCYCLES

Yoshio Ban*, Takeshi Wakamatsu, Miwako Mori, Takeshi Ohnuma and Kiyoshi Yoshida
Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo, 060 Japan

1. The utilization of organometallic compounds

We have recently reported the new synthesis of benzolactams by palladium catalyzed amidation. The insertion of carbon monooxide toward o-bromo-alkylaminobenzene (**1**) easily occurred under mild condition in an atmospheric pressure of carbon monooxide at 100° by use of a catalystic amount of $Pd(OAc)_2$ and PPh_3 with a tertiary amine to afford five, six and seven membered benzolactams (**2**, n = 1— 3) in good yields. The method was applied to the synthesis of a natural alkaloid, sendaverine (**3**).

Furthermore, an extention of this method was made to the synthesis of benzolactones of five, six and seven membered rings under a similar condition (**4** → **5**).