

PL 7

RELATIONS BETWEEN THE STRUCTURE AND REACTIVITY OF BIS-QUINOLIZIDINE DERIVATIVES AND OTHER CYCLIC DIAMINES

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PL 8

RECENT SYNTHESIS OF HETEROAROMATIC AMINES BY CYCLIZATIONS OF NITRILES

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Syntheses of heterocyclic amines with last step being a nucleophilic addition onto the nitrile group can be carried out in different ways. A survey will be given of convenient syntheses by means of the THORPE-ZIEGLER-cyclization and the intramolecular FRIEDEL-CRAFTS-reaction starting from nitriles having an active methylene group. The resulting heterocyclic compounds are o-amino carboxylic acid derivatives and o-amino ketones, respectively. They can easily undergo e.g. cyclic condensations yielding condensed heterocyclic systems.

The intermediate step of the first type is mostly an alkylation of unsaturated β - or aromatic o-mercapto-, -hydroxy- and -aminonitriles by α -halogen carbonyl compounds (or the reaction of heteroaromatic o-chloro nitriles with α -mercapto or α -amino carbonyl compounds having an α -methylene group). The intermediates of both types are derived from malononitrile and other cyanoacetic derivatives or from cyanomethylketones or from cyanamide too.

In particular the simple syntheses of the following heterocyclic systems will be described: heterocondensed 3-amino-thiophenes e.g. thienopyridines and thienoisothiazoles from o-mercaptionitriles, special 3-amino-furans, 3-amino-benzofurans and 3-amino-furapyridines from o-hydroxy nitriles, 3-amino-pyrroles from α -arylaminomethylene nitriles, 4-amino-isoxazoles from α -oximino-nitriles, 4-amino-imidazoles from arylamino-methylenecyanamides, 4-amino-pyrazoles from α -arylhydrazononitriles, 3-amino-indoles and 3-amino-thienopyrroles from o-aminonitriles. 4-aminoisothiazoles can be obtained from α -(O-tosyloximino)-nitriles and α -mercapto carbonyl compounds.

Compared to it examples for analogous syntheses of six-membered heterocyclic rings are rarely.

In the presence of aluminium chloride arylaminomethylene cyanoacetic derivatives undergo cyclization yielding 4-amino-quinolines. Analogously 4-aminothienopyridines can be synthesized from thienyl-2-aminomethylenemalononitriles 4-amino-cinnolines from α -arylhydrazononitriles and 4-amino-quinazolines from arylamino-methylenecyanamides.

Advances in the reactions of ylide-nitriles with elemental sulphur to form 2-amino-thiophenes and 2- and 5-amino-thiazoles will be mentioned briefly.