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

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RECENT SYNTHESSES 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 a-amino carboxylic acid derivatives and a-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 ε- or aromatic α-mercapto- and α-aminoesters by α-halogen carboxyl compounds (or the reaction of heterocyclic α-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. thiophenopyridines and thiophenothiazines from α-mercapto nitriles, special 3-amino-furans, 3-amino-benzofurans and 3-amino-furanopyridines from α-hydroxy nitriles, 3-amino-pyrazoles from α-aminomethylene nitriles, 4-amino-imidazoles from aminomethylene cyanamides, 4-amino-pyrazoles from α-arylhydroxanitrioles, 3-amino-indoles and 3-amino-thiophenopyridines from α-amino nitriles. 4-amino-thiazolozoles can be obtained from α-(D-oxo)thiazoline)-nitriles and α-mercaptop carbonyl compounds.

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

In the presence of aluminium chloride alylamino-methylene cyanoacetic derivatives undergo cyclization yielding α-amino-quinolines. Analogously 4-amino-thienopyridines can be synthesized from thiophen-2-amidomethyleneaminonitriles 4-amino-cinnolines from α-arylhydroxanitrioles and 4-amino-quinolizones from aminomethylene cyananilides.

Advances in the reactions of yliden-nitriles with elemental sulphur to form 2-amino-thiophenes and 2-and 3-amino-thiazoles will be mentioned briefly.