REACTIVITY OF N-SUBSTITUTED AZAAROMATICS

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In the present review dealing with the reactivity of N-substituted azaaromatics their reduction as well as reactions proceeding on ring carbon atoms and on nitrogen atoms are described; also the reactivity of porphyrins and of complexes possessing these systems is reported.

N-Substituted azaaromatics deserve attention in view of their interesting reactivity [1-10] and biological activities [11-16]; they may serve as intercalators of nucleic acids, this fact being connected with the search for antineoplastic agents [17-19]. These compounds find application in redox systems [20-26] promising in the study of biomimetic processes [27, 28] and in solar energy conservation and storage [29, 30]; some among them may be used in dyes [31-34] and surfactants [35-38]. Polymers possessing such systems show interesting properties and inclusion complexes where N-substituted azaaromatics play the role of a host or of a guest may be used in molecular electronic devices [43-46].

N-Substituted azaaromatics are widely applied in organic syntheses [47-50]; their cyclization reactions [51-55] and especially cycloaddition reactions of ylides generated from these salts [56-63] are convenient approaches to polycyclic systems, often difficult to obtain on other routes.

As cyclization reactions of N-substituted azaaromatics are a large topic, they are not included here.

The present review, a continuation of our former reviews [64-67] and experimental papers [60-63, 68-70] deals with the reactivity of N-substituted azaaromatics.

There will be described:
1) reduction of N-substituted azaaromatics,
2) reactions of N-substituted azaaromatics proceeding on ring carbon atoms and on substituents at the latter,
3) reactions of N-substituted azaaromatics proceeding on nitrogen atom and on substituents at the latter,
4) reactions of porphyrins bearing N-substituted azaaromatic moieties,
5) reactions of complexes of N-substituted azaaromatics.

1. REDUCTION OF N-SUBSTITUTED AZAAROMATICS

From numerous reduction reactions of N-substituted azaaromatics leading to dihydro- [47, 71-73], tetrahydro- [74, 75], or hexahydroderivatives [74-77] chosen examples will be described.

The results of the reduction of pyridinium salts (I) are strongly dependent on the nature of the reducing agent, e.g., the reaction of I with sodium dithionite affords 1,4-dihydropyridines (II) while the palladium catalyzed hydrogenation gives rise to tetrahydropyridines (III) [78].
An example of the reduction of pyridinium salts yielding 1,2-dihydropyridines is the following reaction [79].

Salts IV reduced with sodium borohydride afford tetrahydropyridines V, useful in the synthesis of monoamine oxidase B inhibitors [80].

The reduction of salts VI with H₂/PtO₂ leads to piperidine derivatives VII [81].

In the study of NAD⁺ models reduction of 1-benzyl-3-cyanoquinolinium ion by phosphonate dianion was examined. The reaction was performed in aqueous propanol; the main product is 1,4-dihydroquinoline VIII with a trace of 1,2-isomer [73, 82].