SYNTHESES AND REACTIONS OF 1,3a,6a-TRIAZAPENTALENES AND GENERAL DISCUSSION OF MECHANISMS OF THE CYCLIZATION REACTION IN HETEROAROMATIC N-IMINES

Hiroshi Koga, Masaaki Hirobe, and Toshihiko Okamoto
Faculty of Pharmaceutical Sciences, University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113

Mesoionic type 1,3a,6a-triazapentalene derivatives were synthesized *via* pyrazole N-imines by the cyclization reaction. 1-Phenacylpyrazole reacted with O-mesitylenesulfonylhydroxylamine to give 2-phenyl-1,3a,6a-triazapentalene(Ia) in a 65.6% yield. 1-Aminopyrazole reacted with chloroacetylacetone to give 2-methyl-3-acetyl-1,3a,6a-triazapentalene in a 57.8% yield, which was readily converted to 2-methyl-1,3a,6a-triazapentalene(Ib) by treating with conc.HCl.

The novel compounds(I) thus obtained are reactive to electrophiles. The reaction of I with acetic anhydride gave 3-acetyl derivatives and, with sodium nitrite in 15% HCl solution, gave 3-nitroso derivatives respectively in quantitative yields.

Dipolar cycloaddition of I with dimethyl acetylenedicarboxylate in benzene afforded diazacyclazines in good yields. The mechanism of this reaction was discussed on the basis of the Frontier Molecular Orbital Theory. Further this theory was applied to the explanation of the selectivity in 1,3-dipolar cycloadditions of various heteroaromatic N-imines with dipolarophiles to provide a persuasive conclusion which agreed with our experimental results previously obtained.