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RING TRANSFORMATION OF 1-AZA-DIBENZO[c,f]BICYCLO[3.3.1]NONA-3,6-DIENE AND RELATED COMPOUNDS

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Reactions of N-methyl quaternary salts(7) of 1-aza-dibenzo[c,f]bicyclo[3.3.1]nona-3,6-diene(2c), which was facilely synthesized in 95% yield by the double-cyclization reaction of N,N-dibenzylaminoacetaldehyde diethylacetal, with strong bases such as potassium t-butoxide, butyl lithium, and sodium hydride(1.5 equiv.) in rather aprotic solvents, were examined, and consequently, 6-aza-6-methyl-dibenzo[b,i]bicyclo[3.2.2]-nona-2,8-diene(9)[a basic skeleton of isopavine alkaloids] was obtained in 85% yield by the reaction with potassium t-butoxide in dioxane at 80°C for 4 hrs. In contrast to such Stevens rearrangement, 1-aza-1-methyl-5-methylene-dibenzo[c,f]octa-3,6-diene (8) was provided as a sole product in 55% yield by the reaction of 7 with a large excess(50 equiv.) of potassium hydroxide in water at refluxing temperature. As a mechanistic consideration, Stevens rearrangements of N-methyl quaternary salts of both 2c, of which a benzene ring was substituted with a chlorine atom, para to the benzylic position undergoing hydrogen abstraction, and 1-aza-5,9-dimethyl-dibenzo[c,f]bicyclo-[3.3.1]nona-3,6-diene(4b), were examined.

In an application of the modified Stevens rearrangement, (±)- amurensinine and (±)-reframine were derived from the reaction of N-methyl quaternary salt of the double cyclized product of N-(3,4-dimethoxy)benzyl-N-(3,4-methylenedioxy)benzylaminoacetaldehyde diethylacetal. Further, 8, derived from Hofmann degradation of N-methyl quaternary salt of 2c, was refluxed in acetic acid and treated with perchloric acid affording N-methyl quaternary salt(perchlorate)(19)of 1-aza-5-methyl-dibenzo[c,f]bicyclo [3.3.0]octa-3.6-diene[pyrrolizidine system] in 84% yield. Finally, 19 was transformed to 1,8-dimethyl-8-aza-dibenzo[b,f]bicyclo[3.2.1]octa-2,6-diene(20)[tropane system] in 57% yield, by the reaction with potassium t-butoxide in dioxane.