SYNTHESES AND REACTIONS OF 3-CYANOINDOLIZINES

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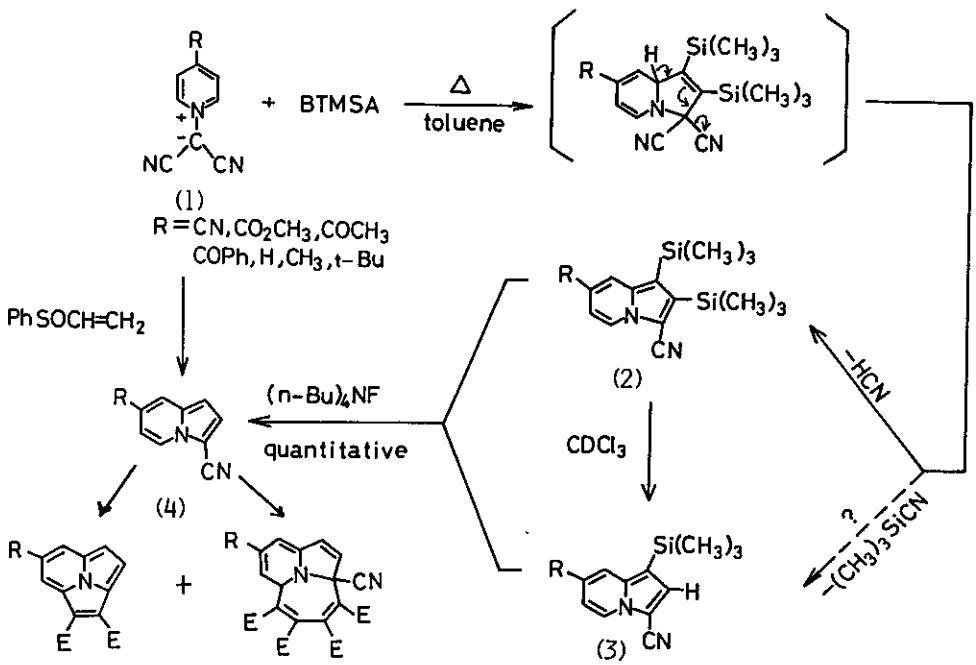
1,3-Dipolar cycloaddition reactions of pyridinium and diazinium dicyanomethylids (1) with bis(trimethylsilyl)acetylene (BTMSA) gave either the 1,2-di(trimethylsilyl)-3-cyanoindolizines (2) or the 1-trimethylsilyl-3-cyanoindolizines (3), or the mixtures of (2) and (3) depending on the substituents and the presence of another nitrogen atom in the pyridine ring. (2) underwent regiospecific detrimethylsilylation at position 2 in $CDCl_3$ or $CHCl_3$ yielding (3). (2), (3), and the 1,2-di(trimethylsilyl)-3-cyanoindolizines from diazinium ylids underwent a quantitative elimination of Me_3Si group(s) under catalytic influence of $(n\text{-}Bu)_4NF$ to afford the 1,2-unsubstituted 3-cyanoindolizines (4). The reactions of (1) with phenyl vinyl sulfoxide gave a linear relationship between the ^{13}C-chemical shifts of 2-position of (1) and the yields of (4), whereas in the reactions of (1) with BTMSA a reverse linear relationship between the ^{13}C-chemical shifts of ylidic carbons of (1) and the yields of (2) and/or (3) was obtained. These results are not inconsistent with the qualitative consideration that the 1,3-dipolar cycloaddition of (1) appears to be rather nonsynchronous and controlled by LUMO[(1)]-HOMO[BTMSA] and HOMO[(1)]-LUMO[phenyl vinyl sulfoxide]. 1,3-Dipolar and/or Michael type cycloadditions of (4) with acetylenes also will be reported.