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CONVENIENT SYNTHESIS OF PYRANOINDOLIZINES

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The alkaline treatments of 1-(2,2-dialkylthio-1-ethoxycarbonylvinyl)-2-picolinium salts or the S-alkylations of 3-(1-alkylthio-1-mercaptomethylene)-2,3-dihydroindolizinones with alkyl iodides gave 3-(1,1-dialkylthiomethylene)-2,3-dihydroindolizin-2-one derivatives in very good yields. These products are very interesting molecules because they are metastable dihydroaromatics and have a very reactive ketene dithioacetal and a enone groups. In order to examine the reactivity of these 3-methylene-2,3-dihydroindolizin-2-ones, we carried out the reactions with the carbanionic species generated by the alkaline treatment of various activated acetate derivatives such as ethyl cyanoacetate, diethyl malonate, ethyl acetoacetate, ethyl benzoylacetate, and ethyl phenylacetate, and found the first formation of a heterocyclic skeleton, pyrano[2,3-b]indolizine.
The structures of 3-methylene-2,3-dihydroindolizin-2-ones and pyrano[2,3-b]indolizines were determined by their physical and spectral analyses and by the mechanistic consideration.