Synthesis of some novel α-cyanoketene-N, S-acetals derived from secondary aliphatic amines and their use in pyrazole synthesis

ABSTRACT

New α-cyanoketene-N,S-acetals 2(a–g) and β-dialkylamine-α-cyanoacrylates 3(g–i) were synthesized in good to excellent yields by the reaction of ethyl 2-cyano-3,3-bis(methylthio)acrylate 1 with secondary aliphatic amines (i.e., N-methylalkyl- and N-ethylalkylamines), and pyrrolidine, in the presence of triethylamine, under reflux in ethanol, for 1–16 h, depending on the amine used. Five N-methylalkyl amines and pyrrolidine yielded exclusively mono-substituted N,S-acetals 2(a–f) in good yields. On the other hand, N-ethylbenzylamine gave a mixture of monosubstituted products including N,S-acetal 2g in 35% yield and the unexpected product ethyl 3-[benzyl(ethyl)amino]-2-cyanoacrylate 3g in 50% yield. N-Ethylcyclohexylamine and N-ethylbutylamine did not produce N,S-acetals and gave only the unexpected products ethyl 2-cyano-3-[cyclohexyl(ethyl)amino]acrylate 3h and ethyl 3-[butyl(ethyl)amino]-2-cyanoacrylate 3i in good yields. The α-cyanoketene-N,S-acetals 2(a–f), 2j, and 2k underwent cyclization with the binucleophile hydrazine in ethanol under reflux to afford substituted pyrazoles 4(a–f), 4j, and 4k in good yields.

Keyword: α-Cyanoketene-N,S-acetals; Pyrazole derivatives; Secondary aliphatic amines.