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METHYLTHIODITHIOLYL IUM REACTIONS WITH 2-BUTENE NITRILES DERIVATIVES

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The 3-methylthio-1,2-dithiolylium including at 5 position a donor substituent, in acetic acid in the presence of pyridine, the 2-methylthio-1,3-dithiolylium ions in methylene chloride-triethylamine, react with the 2-butene nitrile derivatives and lead to the (A) and (B) corresponding 4-dithiolylidene-2-butene nitriles. In contrast ring opening reaction of the 1,2-dithiole is observed when 2-cyano-3-phenyl-2-butene nitrile reacts with the 3-methylthio-4-aryl-1,2-dithiolylium ions in 3 and 5 positions, in methylene chloride-triethylamine. The nucleophilic attack on the 5 position of the dithiolylium ion leads to a 2-cyano-3-phenyl-3-(4-aryl-5-methylthio-2-thienyl) propene nitrile (C), meanwhile the attack on the 3 position leads to a 2-cyano-3-phenyl-3-(4-aryl-3-mercapto-2-thienyl) propene nitrile (D). The proposed structures are established by means of physical methods (IR, NMR, and Mass Spectrometry) and by non ambiguous synthesis. The reactivities of the various sites are explained in function of the electronic and steric effects, furthermore the reaction conditions and the intermediary isolation allow to propose the mechanisms of these reactions.

