Chemical Reactions of 4-Aryl-3-mercapto-3-isothiazoline-5-thiones and 3S- or N-Acyl Derivatives thereof

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The reaction product of the sodium salt of arylcyanodithioacetic acid with sulphur is better formulated as 4-aryl-3-mercapto-3-isothiazoline-5-thione rather than as 4-aryl-3,5-dimercaptoisothiazole. Acylations of the 3-mercaptoisothiazoline with acid chloride in pyridine or alternatively with acid anhydride lead exclusively to 3-acylthio-4-aryl-3-isothiazoline-5-thione. However, the reactions of the 3-mercaptoisothiazoline with aryl isocyanate result in exclusive formation of an N-acylated product.

The reactions of the 3-mercaptoisothiazoline with reactive acetylenes (e.g. dialkyl acetylenedicarboxylate and dibenzoylacetylene) addord 2-[aryl(thiocarbamoyl)-methylene]-1,3-dithiole derivatives, whereas those of the 3-acylthioisothiazoline with the acetylenic ester are accompanied by an S→N acyl migration giving N-benzoyl-[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]arylethanethioamide. The reaction of 4-phenyl-2-phenylcarbamoyl-3-mercapto-3-isothiazoline-5-thione with dimethyl acetylenedicarboxylate gave N-(phenylcarbamoyl)-[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]phenylethanethioamide. ^{13}C Nmr spectra of some of the 1,3-dithioles thus prepared are discussed.

The thiolo-ester-thiono-ester rearrangements of 3-acylthio-4-aryl-3-isothiazoline-5-thione are reported. Treatment of the isothiazoline with alkylating reagents (e.g. diazomethane, methyl iodide, or triethyloxonium tetrafluoroborate) gave 5-alkylthio-4-aryl-3-thioacyloxyisothiazole in good yield, and the reactions with acylating reagents (e.g. acid chloride or acid anhydride) in the presence of boron trifluoride diacetic acid complex yielded 5-acylthio-4-aryl-3-thioacyloxyisothiazole. Such a rearrangement also took place when the isothiazoline was treated with thallous ethoxide. Treatment of the isothiazoline with m-chloroperbenzoic acid (1.1 mol equiv.) gave bis(4-aryl-3-thioacyloxyisothiazol-5-yl) disulphide in high yield, whereas the reaction with the peracid (2 mol equiv.) resulted in the removal of the C-5-substituent as well as the rearrangement producing 4-aryl-3-thioacyloxyisothiazole.