HETEROCYCLISATIONS OF N-ACYLTHIOAMIDES TO BE DERIVED BY THE RING TRANSFORMATIONS OF ISOTHIAZOLES

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Syntheses of heterocycles by means of the ring transformation reactions of isothiazoles have received less attention than they deserve. Reactions of N-acylarylethanethioamides, which are prepared in excellent yields from 3-acylthio-4-aryl- and 4-aryl-2-arylcarbamoyl-3-isothiazoline-5-thiones and possess at least three incipient nucleophilic centres, if performed under appropriate conditions, may be exploited for the syntheses of heterocycles.

4-Aryl-3-chloroacetylthio- and 4-aryl-3-α-chloropropionylthio-3-isothiazoline-5-thiones respectively, when allowed to react with dialkyl acetylenedicarboxylate or dibenzoylacetylene, have been found to afford 4(5H)-thiazolones in good yields. Similarly, 4-aryl-3-β-chloropropionylthio-3-isothiazoline-5-thiones gave 5,6-dihydro-4H-1,3-thiazin-4-ones upon treatment with the acetylenes. The N-haloacylarylethanethioamides to be first formed were not isolated throughout the reactions as a consequence of their rapid intramolecular cyclisations.

Photolysis of N-o-iodobenzoylarylethanethioamide, but not of the corresponding N-o-chlorobenzoyl derivatives, provides an efficient and high yield synthesis of 4H-1,3-benzothiazin-4-ones.

Oxidation of N-acyl- and N-arylcarbamoyl-arylethanethioamides with halogen (Br_2, I_2, or ICl) has been found to provide a good access to 4,5-dihydro-1,3-benzoxazepines, being compatible with a variety of substituents on the benzenoid ring and at C(2).