SYNTHESIS OF 5,6-DIHYDROTHIAZOLO(2,3-b)THIAZOLIUM SALTS AND THEIR REACTION WITH NUCLEOPHILIC REAGENTS

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5,6-Dihydrothiazolo(2,3-b)thiazolium salts which belong to a system of tri-hetero-substituted carbonium ions and seemingly have ambident character react easily with nucleophiles to give various kinds of substituted or rearranged products. The reaction is considered to be initiated by the attack of the nucleophile on the polarized $>C = \overset{+}{N}<$ bond to form an adduct as shown in the following and to proceed through an AE-mechanism. On reaction with a secondary amine an intermediate adduct is isolated and its structure is affirmed by elemental and spectroscopic analyses. Basicity, polarizability and other properties of the reagent determine the subsequent elimination stage of the reaction as follows: (a) cleavage of S_7-C_{7a} bond to form 3-(2-mercaptoethyl)-substituted thiazolines and/or their disulfides, (b) cleavage of S_7-C_{7a} and N-C_5 bonds to form thiirane and 2-substituted thiazoles, and (c) inducement of another attack of the reagent either on C_6 to form 3-(2-substituted-ethyl)-thiazolin-2-thiones or on S_7 to form 2-unsubstituted thiazole, phenyl-2-oxo-thiazolin-3-ylethylthioethyldisulfide and phenyl-2-phenylthioethyl disulfide especially when the reagent is very polarizable and efficient as a leaving group like thiophenolate and dithiocarbamate ions.