# A NEW SKELETAL REARRANGEMENT OF CYCLIC β-HALOALKYLISOTHIOUREAS

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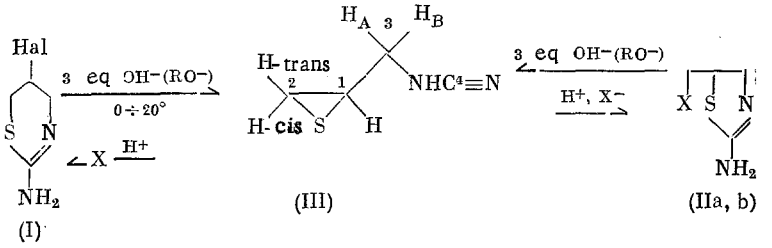
UDC 542.952.1:547.496.3:547.789.1

We are the first to report that the action of excess alkali on isomeric 2-amino-5-halo-5,6-dihydro-4H-1,3-thiazines (I) and 2-amino-5-halomethyl-2-thiazolines (II) leads to their quantitative conversion to N-2,3-epithiopropylcyanamide (III), which is stable in strongly basic media such as NaOH in water, NaOMe in methanol and NaOMe 18-crown-6 in DMF.




X = Hal (IIa), OH, SCN, CN (IIb).

The structure of (III) was demonstrated by $^1H$ NMR (200 MHz) and $^{13}C$ NMR spectroscopy (50 MHz) in 1.0 M NaOD·$D_2O$ in $CD_3OD$ (TMS, δ, ppm) and Raman spectroscopy. $^1H$ NMR: 3.20 d.d.d ($H_B^3$, $J_{H^1H^3_B}$ = 5.0, $JH^2_{cis}H^3_B$ = 0.8, $JH^3_AH^3_B$ = 12.5 Hz), 3.02 m ($H^1$, $JH^1H^2_{trans}$ = 5.3, $JH^1H^2_{cis}$ = 5.8, $J_{H^1H^3_A}$ = 7.5 Hz), 2.83 d.d ($H^3_A$), 2.50 d.d.d ($H^2_{cis}$, $JH^2_{cis}H^2_{trans}$ = 1.2 Hz), 2.21 d.d ($H^2_{trans}$). $^{13}C$ NMR spectrum: 137.04 ($C^4$), 56.47 ($C^3$, $^1J^{13}_{C-H}$ = 139 Hz), 36.68 ($C^1$, $^1J^{13}_{C-H}$ = 169 Hz), 25.22 ($C^2$, $^1J^{13}_{C-H}$ = 169 Hz). The Raman spectrum has a very strong band at 2090 $cm^{-1}$ ($\nu_{C\equiv N}$). In an attempt to isolate (III) and at high temperatures, it readily polymerizes, while the action of acid leads to its quantitative conversion exclusively to (II). In this case, very high selectivity toward halide ions was found for (III). Thus, the product (IIb, X = OH) is formed in water only when halide ions are removed from the reaction sphere using freshly precipitated AgOH. This rearrangement may be used for superfast $S_N$ substitution of the halogen in (II) by another halogen or pseudohalogen and for the alkylation of thiourea. For example, the consecutive addition of 10 eq. NaSNC and 4 eq. aqueous $H_3PO_4$ to 1.0 M hydrobromide (IIa, X = Br) in water and subsequent precipitation of the product with picric acid gives an 85% yield of the picrate of (IIb, X = SCN), mp 187.5°C. Found, %: C 32.98; H 2.30; N 20.48. $C_{10}H_{10}N_6S_2O_7$. Calculated, %: C 32.83; H 2.50; N 20.89. The structures of the substitution products in all cases were demonstrated by IR and NMR spectroscopy. The rearrangmeent does not proceed if the 2-amino group in (I) and (II) has two alkyl substituents.

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 0568-5230/86/3503-0676$12.50 