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A NOVEL SYNTHESIS OF SOME 2,3-DIHYDRO-1,4-THIAZINE DERIVATIVES

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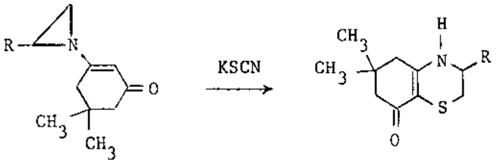
Abstract - The KSCN catalysed isomerization of N-vinylaziridines 1 and 2 afforded 2,3-dihydro-1,4-thiazine derivatives.

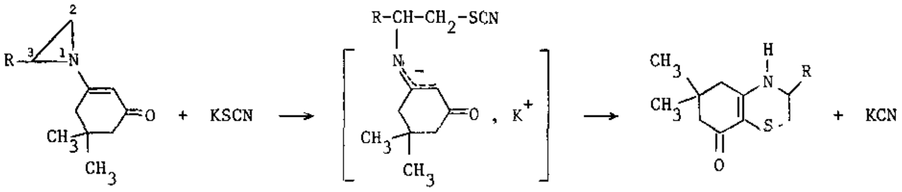
In a previous publication[1] we have reported the nucleophilic rearrangement of 2-cyano- and 2-ethoxycarbonyl-1-vinylaziridines leading predominantly to α,β-dehydro-α-amino acid derivatives. This reaction does not however occur with 2-unfunctionalized 1-vinylaziridines such as 1 and 2 where the nucleophilic rearrangement takes an entirely different but equally interesting course. Isomerization was carried out by refluxing a dimethoxyethane solution of compound 1 with an equimolecular amount of KSCN for 40 h under argon. A crystalline solid was isolated and identified as the 2,3-dihydro-1,4-thiazine 3 ; in the same way the thiazine derivative 4 was obtained from the aziridine 2 :



1 (R = H)
2 (R = CH_3)

3
4

The structure of 3 and 4 was determined on the basis of their physical and spectral data. The formation of these compounds is best understood as involving a nucleophilic attack at C-2 followed by an intramolecular displacement reaction as illustrated in scheme 1 :



Scheme 1

KCN was indeed isolated and characterized as its iron (III) ferrocyanide derivative.
These results are in contrast with the potassium thiocyanate catalysed isomerization of aziridines reported in the litterature[2]. This reaction can constitute a simple synthesis of 2,3-dihydro-1,4-thiazine derivatives which otherwise are generally prepared by ring expansion of the thiazolidine ring[3].

EXPERIMENTAL

Melting points are uncorrected. Uv spectra were run on a Beckman DU-8 spectrophotometer. Nmr spectra were recorded on a Brucker WP 200 SY spectrometer ; chemical shifts are in parts per million (δ) relative to tetramethylsilane ; coupling constants (J values) are in Hertz (Hz).

General procedure for the rearrangement of 1 and 2. A solution of 1-vinylaziridine (1 g) and KSCN (molar ratio 1:1) in dimethoxyethane (20 ml) was refluxed under argon for 40 h. The precipitate that separated on standing at room temperature for 48 h was filtered off and purified.

Isolation of 3. Recrystallization from absolute ethanol gave a 65% yield of 3 as white crystals mp 219°C ; uv (C_2H_5OH, log ε) 290 (4.39) ; ms m/e 197 (100 $M^{+\cdot}$) 141 (47 $M^{+\cdot}$ - $(CH_3)_2C{=}CH_2$) 114 (13) 113 (28 141 - CO) 85 (16) 83 (17), exact mass 197.08523 (calcd. for $C_{10}H_{15}NOS$ 197.08743) ; nmr ($CDCl_3$) 1.07 (s 6H) 2.19 (s 2H) 2.21 (s 2H) 2.89 (t 2H J=6.59) 3.455 (t 1H J=6.59) 3.485 (t 1H J=6.59) 5.13 (s large 1H).

Isolation of 4. Recrystallization from absolute ethanol gave a 40% yield of 4 as white crystals mp 229°C ; uv (C_2H_5OH, log ε) 333 (4.13) 228 (3.91) ; ms m/e 211 (100 $M^{+\cdot}$) 196 (31 $M^{+\cdot}$ - $^{\cdot}CH_3$) 155 (19 $M^{+\cdot}$ - $(CH_3)_2C{=}CH_2$) 85 (13) 83 (13), exact mass 211.102826 (calcd. for $C_{11}H_{17}NOS$ 211.10308) ; nmr ($CDCl_3$) 1.07 (s 3H) 1.08 (s 3H) 1.33 (d 3H J=6.35) 2.26 (s 2H) 2.30 (s 2H) 2.56 (dd 1H J=7.32 J=12.70) 2.85 (dd 1H J=2.69 J=12.70) 3.74 (m 1H) 4.59 (s 1H). The ethanolic solution was concentrated under reduced pressure. The residue thus obtained was found to be KCN, which was characterized as its iron (III) ferrocyanide derivative, as was also the residue undissolved in hot ethanol.

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