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SYNTHESIS OF NOVEL HETEROCYCLIC SYSTEMS. 2,3-DIHYDROPYRIDO[1,2-*b*][1,4,2]OXASELENAZIN-5-IUM

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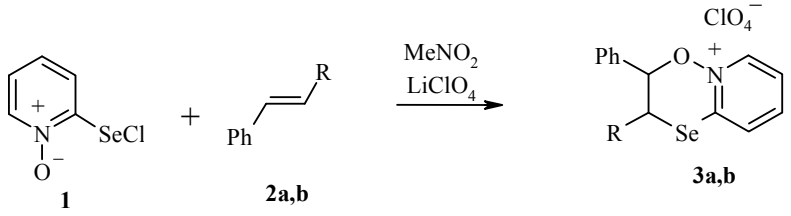
We have recently proposed a method for the synthesis of the novel 2,3-dihydropyrido[1,2-*b*][1,4,2]-oxathiazinium-5 heterocyclic system based on the heterocyclization of 2-chlorosulfenyl-1-pyridine 1-oxide with unsaturated compounds [1-4]. As far as we known, analogous selenium containing heterocycles have not been prepared to this time. In this connection, we have now synthesized 2-chloroselanyl-1-pyridine 1-oxide (**1**) and studied its reaction with styrene (**2a**) and *trans*-stilbene (**2b**). We have found that the reaction of the selanyl chloride **1** with the alkenes **2a,b** in nitromethane in the presence of an equimolar amount of lithium perchlorate occurs by a polar cycloaddtion [5] to give the 2,3-dihydropyrido[1,2-*b*][1,4,2]oxaselenazin-5-ium derivatives **3a,b** in 76 and 82% yield respectively.



1 **2a,b** **3a,b**

2, 3 a R = H, **b** R = Ph

^{1}H NMR spectroscopy was used to show that the reaction studied is regio- and stereospecific.

IR spectra were recorded on a Shimadzu IR-Prestige-21 spectrometer for KBr tablets. ^{1}H NMR spectra were taken on a Bruker AM-300 instrument (300 MHz) using DMSO-d_6 and with TMS as internal standard.

2-Chloroselanyl-1-pyridine 1-Oxide (1). A solution of sulfuryl chloride (0.27 g, 2 mmol) in dichloromethane (15 ml) was added to a solution of 2-selanyl-1-pyridine 1-oxide (0.35 g, 2 mmol) (prepared by method [6]) in dichloromethane (20 ml) at 20ºC. After 1 h it was filtered to give compound **1** (0.33 g, 80%) and the filtrate was evaporated *in vacuo*. Recrystallization of the residue from dichloromethane gave a further 0.06 g (15%) of compound **1**; mp 160-162ºC. IR spectrum, ν, cm^{-1}: 1617, 1462, 1423, 1254, 1151, 836, 748, 621. Found, %: C 24.43; H 1.83; N 6.65. $C_5H_4ClNOSe$. Calculated, %: C 24.81; H 1.93; N 6.72.

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Reaction of 2-chloroselanyl-1-pyridine 1-Oxide (1) with the Unsaturated Compounds 2a,b. A solution of $LiClO_4$ (0.05 g, 0.5 mmol) in nitromethane (10 ml) and a solution of the unsaturated compound **2a,b** (0.5 mmol) in nitromethane (5 ml) were added to a solution of selanyl chloride **1** (0.10 g, 0.5 mmol) in nitromethane (20 ml). After 1 h the LiCl was filtered off and the filtrate was evaporated *in vacuo*. Recrystallization of the residue from dichloromethane gave compounds **3a,b**.

3-Phenyl-2,3-dihydropyrido[1,2-*b*][1,4,2]oxaselenazin-5-ium Perchlorate (3a). Yield 76%; mp 130-132ºC. IR spectrum, ν, cm^{-1}: 1617, 1470, 1088, 757, 702, 623. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.77 (1H, dd, *J* = 11.7 and *J* = 2.9, H-2); 4.23 (1H, t, *J* = 11.7, H-2); 5.89 (1H, dd, *J* = 11.7 and *J* = 2.9, H-3); 7.45-7.65 (5H, m, C_6H_5); 7.87 (1H, dt, ^3J = 6.3 and *J* = 3.1, H-8); 8.43 (2H, m, H-7,9); 9.14 (1H, d, ^3J = 6.5, H-6). Found, %: C 41.21; H 3.15; N 3.59. $C_{13}H_{12}ClNO_5Se$. Calculated, %: C 41.46; H 3.21; N 3.72.

***trans*-2,3-Diphenyl-2,3-dihydropyrido[1,2-*b*][1,4,2]oxaselenazin-5-ium Perchlorate (3b)**. Yield 82%; mp 165-167ºC. IR spectrum, ν, cm^{-1}: 1618, 1469, 1092, 755, 707, 625. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.02 (1H, d, ^3J = 10.4, H-2); 6.29 (1H, d, ^3J = 10.4, H-3); 7.30-7.50 (10H, m, $2C_6H_5$); 7.83 (dt, ^3J = 6.4 and *J* = 3.1, H-8); 8.33 (2H, m, H-7,9); 9.24 (1H, d, ^3J = 6.8, H-6). Found, %: C 50.29; H 3.47; N 3.02. $C_{19}H_{16}ClNO_5Se$. Calculated, %: C 50.41; H 3.56; N 3.09.

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