

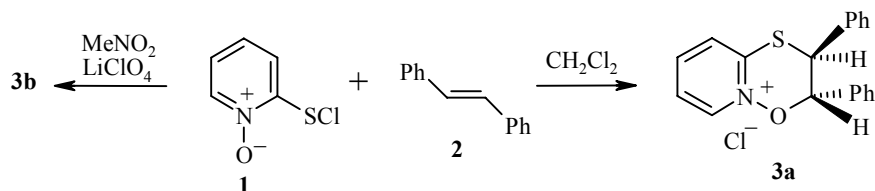
## HETEROCYCLIZATION IN THE REACTION OF 2-CHLOROSULFENYLPYRIDINE 1-OXIDE WITH *trans*-STILBENE

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We have recently shown that the cycloaddition of hetarenesulfenyl chlorides, containing a potentially nucleophilic nitrogen atom, to unsaturated compounds may serve as an efficient method for the synthesis of S,N-heterocycles [1-5].

In the present work, we studied the feasibility of using 2-chlorosulfenylpyridine 1-oxide (**1**), obtained by the action of sulfonyl chloride on 2-mercaptopyridine 1-oxide according to a well known procedure for the chlorination of thiols [6], to give ring formation in reactions with alkenes. We found that the reaction of sulfenyl chloride **1** with *trans*-stilbene **2** in methylene chloride and nitromethane in the presence of lithium perchlorate gives cyclization products due to ring closure by the N-oxide oxygen atom, namely, *trans*-2,3-diphenyl-2,3-dihydropyrido[1,2-*b*]oxathiazinium chloride (**3a**) (92% yield) and perchlorate (**3b**) (95% yield).



$^1\text{H}$  NMR spectroscopy showed that the 1,2-addition product is formed in the reaction of sulfenyl chloride **1** with alkene **2**. This cycloaddition product is then converted to heterocycle **3a**. On the other hand, such an intermediate could not be detected in the lithium perchlorate–nitromethane system. The formation of the condensed heterocyclic system **3b** proceeds rapidly, perhaps due to the cycloaddition of the sulfenylating reagent at the double bond.

**Chloride 3a.** A solution of alkene **2** (1.80 g, 10 mmol) in methylene chloride (15 ml) was added to a solution of sulfenyl chloride **1** (1.61 g, 10 mmol) in methylene chloride (20 ml). After 168 h, the precipitate was filtered off to give 1.95 g (57%) of compound **3a**. The filtrate was evaporated in vacuum. Recrystallization of the residue from chloroform gave an additional 1.20 g (35%) of compound **3a**; mp 183-185°C. IR spectrum (KBr),  $\nu$ ,  $\text{cm}^{-1}$ : 3132-2928, 1604, 1560, 1468, 1278, 1140, 918, 848, 784, 700.  $^1\text{H}$  NMR spectrum (500 MHz, DMSO- $d_6$ ),  $\delta$ , ppm ( $J$ , Hz): 9.23 (1H, d,  $^3J = 6.7$ , Het); 8.32 (2H, m, Het); 7.81 (dt,  $^3J = 6.7$ ,  $J = 3.0$ , Het); 7.61-7.24 (10H, m, 2Ph); 6.29 (1H, d,  $^3J = 10.4$ , CHO); 6.02 (1H, d, CHS). Found, %: C 66.34; H 4.61; N 4.03; S 9.25.  $\text{C}_{19}\text{H}_{16}\text{ClNOS}$ . Calculated, %: C 66.76; H 4.72; N 4.10; S 9.38. Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 305 [ $\text{M}^+ - \text{HCl}$ ] (9), 200 (100), 167 (23), 105 (32), 77 (23), 51 (17), 38 (6), 36 (18).

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**Perchlorate 3b.** A solution of lithium perchlorate (1.06 g, 10 mmol) in nitromethane (30 ml) and a solution of alkene **2** (1.80 g, 10 mmol) in nitromethane (15 ml) were added to a solution of sulfonyl chloride **1** (1.61 g, 10 mmol) in nitromethane (20 ml) at 20°C. After 1 h, the precipitate of LiCl was filtered off and the filtrate was evaporated in vacuum. Recrystallization of the residue from 3:1 chloroform–acetonitrile gave 3.86 g (95%) of compound **3b**; mp 245-247°C (dec). IR spectrum (KBr),  $\nu$ ,  $\text{cm}^{-1}$ : 3044, 1600, 1560, 1470, 1276, 1144, 848, 768, 696, 622, 1082 ( $\text{ClO}_4$ ). Found, %: C 55.99; H 3.89; N 3.37; S 7.71.  $\text{C}_{19}\text{H}_{16}\text{ClN}_5\text{OS}$ . Calculated, %: C 56.23; H 3.97; N 3.45; S 7.90.

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