SYNTHESIS OF THIENO[2,3-b]- AND SELENOPHENO[2,3-b] FURAN

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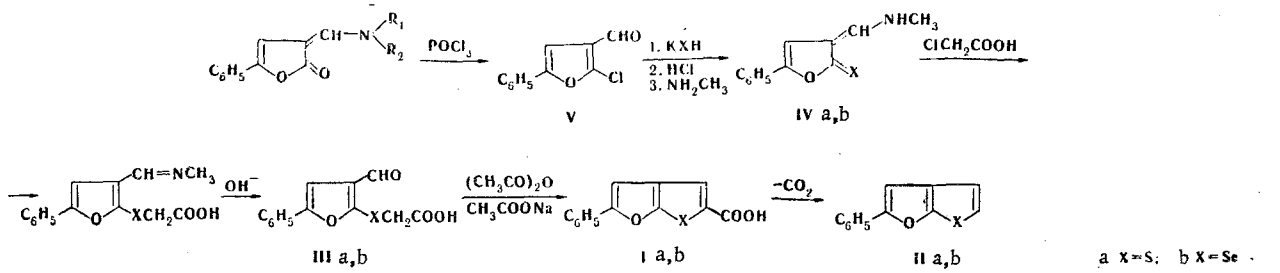
We have synthesized new heterocyclic systems – 2-phenylthieno[2,3-b]- and 2-phenylselenopheno[2,3-b]furan (IIa,b) – by decarboxylation of 2-phenylthieno[2,3-b]- and 2-phenylselenopheno[2,3-b]furan-5-carboxylic acids (Ia,b). Compounds Ia,b are formed in the cyclization of the corresponding 5-furylthio(or seleno)acetic acids (IIIa,b) in acetic anhydride in the presence of sodium acetate, together with IIa,b, in a ratio of ~ 2:1. In alkaline media, because of the high electrophilicity of the carbon in the 5 position, the $-XCH_2COOH$ residue is replaced by a hydroxyl group to give 2-phenyl-4-formyl-5-hydroxyfuran [3], and cyclization of IIIa,b is not observed (see [1,2]). Compounds IIIa,b were synthesized from the enamines of the 4-formyl derivatives of thio- and selenofurans (IVa,b). 2-Phenyl-4-formyl-5-chlorofuran (V) was obtained by the method in [4] from disubstituted enamines.

EXPERIMENTAL

2-Phenyl-4-formyl-5-furylthio(seleno)acetic Acids (IIIa,b). A mixture of 0.01 mole of IV and 0.011 mole of perchloric acid was refluxed in benzene for 2 h, after which the precipitate was removed by filtration, washed with chloroform, and extracted with 10% aqueous sodium carbonate solution. The extract was acidified, and the resulting precipitate was recrystallized from benzene to give IIIa [83% yield, mp 129°, λ_{max} (ethanol) 296 nm (log ε 4.53). Found: S 12.5%. $C_{13}H_{10}O_4S$. Calculated: S12.2%] and IIIb [87% yield, mp 128°, λ_{max} (ethanol) 296 nm (log ε 4.09). Found: C 50.2; H 3.5%. $C_{13}H_{10}O_4Se$. Calculated: C 50.5; H 3.2%.].

2-Phenylthieno[2,3-b]- and 2-Phenylselenopheno[2,3-b]furans (IIa,b). A 0.01-mole sample of III was refluxed in a mixture of 20 ml of acetic anhydride and 2 g of sodium acetate for 1 h. The precipitated substance was extracted several times with boiling petroleum ether, the solvent was removed by distillation, and the residue was recrystallized from aqueous ethanol (IIa,b). The residue remaining after extraction was dissolved in water, and the solution was acidified. The precipitate was removed by filtration and crystallized from ethanol (Ia,b). Compound Ia: 46% yield, mp 277°, λ_{max} (ethanol) 315 nm (log ε 4.27). Found: C 64.3; H 3.8; S 13.3%. $C_{13}H_8O_3S$. Calculated: C 63.8; H 3.8; S 13.1%; compound Ib was not isolated from the reaction mass. Compound IIa: 21% yield, mp 81°, λ_{max} (ethanol) 297 nm (log ε 4.37). Found: S 16.5%. $C_{12}H_8OS$. Calculated: S 16.0%. Compound IIb: 17% yield, mp 102°, λ_{max} (ethanol) 299 nm (log ε 4.50). Found: C 58.5; H 3.6%. $C_{12}H_8OSe$. Calculated: C 58.3; H 3.2%.



2-Phenyl-4-methylaminomethylene-5-thio(seleno)furanones (IVa,b). Compound IVa: 91% yield, mp 160° (from benzene), λ_{max} (ethanol) 432 nm (log ε 4.10). Found N 6.6; S 14.7%. $C_{12}H_{11}NOS$. Calculated: N 6.5; S 14.9%. Compound IVb: 86% yield, mp 138° (from benzene), λ_{max} (ethanol), 452 nm (log ε 4.01). Found: N 5.3%. $C_{12}H_{11}NOSe$. Calculated: N 5.3%.

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2-Phenyl-4-formyl-5-chlorofuran (V). This compound was obtained in 84% yield and had mp 74° (from cyclohexane) and λ_{max} 278 nm (log ε 4.27). Found: Cl 17.1%. $C_{11}H_7ClO_2$. Calculated: Cl 17.2%.

LITERATURE CITED

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