ENAMINES OF FORMYL DERIVATIVES OF THIO- AND SELENOPYRROLONE AND SYNTHESIS OF THIENO- AND SELENOPHENO[2,3-b]PYRROLES

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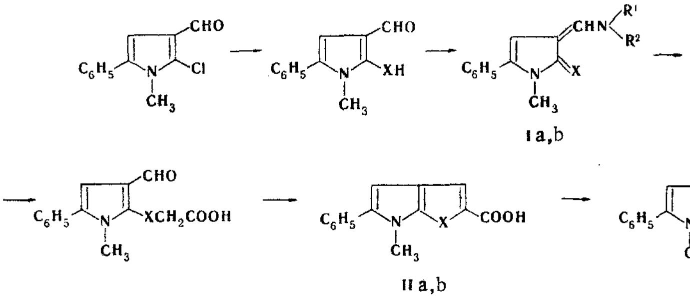
We have realized the synthesis of thieno- and selenopheno[2,3-b]pyrroles by alkylation of enamines of 1-methyl-2-phenyl-5-thio- and 5-selenopyrrolones (Ia, b) with chloroacetic acid. The enamines were obtained by replacement of the chlorine atom in 1-methyl-2-phenyl-4-formyl-5-chloropyrrole [1] with a mercaptide or selenide ion and subsequent treatment of the reaction products with the hydrochlorides of the appropriate amines. According to the IR, UV, and PMR spectra, Ia and Ib exist in the enamine form. Reaction of Ia and Ib with chloroacetic acid gave the corresponding pyrrole-X-acetic acid derivatives, which cyclize in the presence of alkali to give 1-methyl-2-phenylthieno- and 1-methyl-2-phenylselenopheno[2,3-b]pyrrole-5-carboxylic acids (IIa and IIb). These acids are decarboxylated to 1-methyl-2-phenylthieno- and 1-methyl-2-phenylselenopheno[2,3-b]pyrrole (IIIa and IIIb) when they are heated above their melting points.



I, II, III a X=S; b X=Se; I a $R^1=R^2=CH_3$; b $R^1=H$, $R^2=CH_3$

Compound IIa was also obtained by reaction of 1-methyl-2-phenyl-4-formyl-5-chloropyrrole with thioglycolic acid in aqueous alcoholic alkali.

It was found by potentiometry that acid IIb (pK_a 5.78 ± 0.03) is weaker than IIa (pK_a 5.64 ± 0.03). A bathochromic shift of the long-wave absorption band by 15 and 4 nm, respectively, is observed in the UV spectra of IIb and IIIb as compared with the spectra of the corresponding sulfur-containing compounds.

EXPERIMENTAL

The IR spectra of chloroform solutions were obtained with an IKS-22 spectrometer, while the UV spectra of ethanol solutions were obtained with an SF-8 spectrometer.

Enamines of Thio- and Selenopyrrolone (Ia, b). An alcohol solution of 1-methyl-2-phenyl-4-formyl-5-chloropyrrole was treated with a threefold excess of an aqueous solution of potassium hydrosulfide or hydroselenide, after which the mixture was poured into water and neutralized to pH 7. The mixture was then treated with a four- to fivefold excess of the hydrochloride of the appropriate amine. Compound Ia was described in [1]. Compound Ib was obtained in 80% yield and had mp 176-177° (from benzene–heptane). UV spectrum: λ_{max} 430 nm (log ε 4.76). Found: C 56.6; H 5.1; N 10.0%. $C_{13}H_{14}N_2Se$. Calculated: C 56.4; H 5.1; N 10.0%.

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1-Methyl-2-phenylthieno- and 1-Methyl-2-phenylselenopheno[2,3-b]pyrrole-5-carboxylic Acid (IIa, b). A solution of Ia or Ib was refluxed in benzene with an equimolecular amount of chloroacetic acid for 2 h, after which it was cooled, and the reaction product was isolated and refluxed with 20% NaOH for 3 h. Acidification of this mixture gave IIa and IIb. Compound IIa was obtained in 52% yield and had mp 223-224° (from ethanol). UV spectrum: λ_{max} 315 nm (log ε 4.49). IR spectrum: 1658 cm^{-1}. Found: N 5.2; S 12.3%. $C_{14}H_{11}NO_2S$. Calculated: N 5.4; S 12.4%. Compound IIb was obtained in 44% yield and had mp 226° (from ethanol). UV spectrum: λ_{max} 330 nm (log ε 4.15). IR spectrum: 1662 cm^{-1}. Found: C 55.4; H 3.6; N 4.4%. $C_{14}H_{11}NO_2Se$. Calculated: C 55.3; H 3.6; N 4.6%.

1-Methyl-2-phenylthieno- and 1-Methyl-2-phenylselenopheno[2,3-b]pyrroles (IIIa, b). Compounds IIa,b were heated 3-5° above their melting points until CO_2 evolution ceased. Compound IIIa was obtained in 60.5% yield and had mp 119-120° (from aqueous ethanol). UV spectrum: λ_{max} 295 nm (log ε 4.04). Found: N 6.6; S 15.0%. $C_{13}H_{11}NS$. Calculated: N 6.6; S 15.1%. Compound IIIb was obtained in 77% yield and had mp 126° (from aqueous ethanol). UV spectrum: λ_{max} 299 nm (log ε 4.16). Found: N 5.3%. $C_{13}H_{11}NSe$. Calculated: N 5.4%.

LITERATURE CITED

1. I. Ya. Kvitko and N. B. Sokolova, Khim. Geterotsikl. Soedin., 791 (1972).