SYNTHESIS OF 5,6-POLYMETHYLENESELENOPYRYLLIUM SALTS

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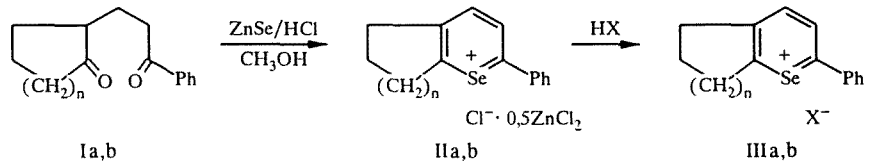
According to the literature the only known example of a tetrahydroselenochromylium or 5,6-trimethyleneselenopyryllium salt is 2,4-diphenyl-5,6-trimethyleneselenopyryllium perchlorate [1] obtained in negligible yield by a method analogous to that in [2].

We have developed an original method for the preparation of 2-phenyl-5,6,7,8-tetrahydroselenochromylium salts (IIa, IIIa, IIIb) and 2-phenyl-5,6-trimethyleneselenopyryllium chlorozincate (IIb). Salts IIa and IIb were obtained by treating the semicyclic 1,5-diketones Ia and Ib with zinc selenide and hydrogen chloride in methanol. Salts IIIa and IIIb were prepared from IIa by ion exchange.

Considering the high yields of salts IIa and IIb it appears that the zinc chloride formed during the reaction facilitates the formation of a stable counterion and catalyses the heterocyclisation. This is confirmed by the observation that zinc chloride catalyses the reaction between carbonyl and selenols [3].



Ia,b IIa,b IIIa,b

Ia, IIa, IIIa,b n = 2; Ib, IIb n = 1; X = ClO_4, BF_4

Diketone Ia or Ib (10 mmol) and zinc selenide (1.58 g, 11 mmol) were added to a solution of hydrogen chloride (12 M) in absolute methanol (30 ml). The salt was filtered off after 2 h and washed with ether.

Salts IIIa and IIIb were obtained by heating salt IIa with an excess of 57% $HClO_4$ or 40% HBF_4 on a water bath.

2-Phenyl-5,6,7,8-tetrahydroselenochromylium chlorozincate(IIa). Yield 65%. mp 160-161°C. ^{1}H NMR spectrum: 2.05-2.18 (4H, m, 6 + 7-CH_2), 3.18-3.29 (2H, m, 5-CH_2), 3.43-3.54 (2H, m, 8-CH_2), 7.68-7.90 (5H, m, C_6H_5), 8.64 (2H, br. s, cat.).

2-Phenyl-5,6-trimethyleneselenopyryllium chlorozincate(IIb). Yield 41%. mp 111-113°C. ^{1}H NMR spectrum: 1.99-2.18 (2H, m, 6-CH_2), 3.08 (2H, t, 5-CH_2, J = 7.2 Hz), 3.30 (2H, t, 7-CH_2, J = 7.3 Hz), 7.22-7.52 (5H, m, C_6H_5), 8.17 (1H, d, 3-H, *J* = 9.1 Hz), 8.38 (1H, d, 4-H, J = 9.1 Hz).

2-Phenyl-5,6,7,8-tetrahydroselenochromylium perchlorate(IIIa). Yield 98%. mp 137-140°C. ^{1}H NMR spectrum: 1.87-1.99 (4H, m, 6 + 7-CH_2), 3.20-3.43 (4H, m, 8 + 5-CH_2), 7.72-7.84 (5H, m, C_6H_5), 8.56 (2H, br. s, cat.).

2-Phenyl-5,6,7,8-tetrahydroselenochromylium tetrafluoroborate (IIIb). Yield 97%. mp 137-140°C. ^{1}H NMR spectrum: 1.74-1.80 (4H, m, 6 + 7-CH_2), 2.93-3.13 (4H, m, 5 + 8-CH_2), 7.37-7.50 (5H, m, C_6H_5), 8.20 (2H, br. s, cat.).

^{1}H NMR spectra were recorded in a 1:1 mixture of CD_2Cl_2 and CF_3COOD.

Elemental analysis results agreed with calculated values.

Chemistry Research Institute, Chernyshevskyi Saratov State University, Saratov 410026. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, p. 569, April, 1994. Original article submitted April 22, 1994.

0009-3122/94/3004-0503$12.50

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