6H-Dipyrido[2,1-b:1',2'-e]-1,3,5-selenadiazinium
Dibromide: A Dipyrido Analogue of Selenaxanthene

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2,2'-Selenodipyridine, 6H-Dipyrido[2,1-b:1',2'-e]-1,3,5-selenadiazinium Dibromide

2,2'-Selenodipyridine on reaction with dibromomethane affords the new polycyclic system, 6H-dipyrido[2,1-b:1',2'-e]-1,3,5-selenadiazinium dibromide.

Reaction of 2,2'-thiodipyridine with dibromomethane results in the formation of the ring system (1) which contains the unusual feature of a methylene group flanked by two quaternary pyridine nitrogen atoms. In contrast, reaction of 2,2'-bipyridyl, di-(2-pyridyl)methane, 2,2'-iminodipyridine and 2,2'-oxydipyridine with dibromomethane does not result in the formation of the corresponding diquaternary ring system. We have now succeeded, however, in preparing the selenium analogue of (1), 6H-dipyrido[2,1-b:1',2'-e]-1,3,5-selenadiazinium dibromide (2).

2,2'-Selenodipyridine (3), which has not been reported hitherto, was prepared by reacting equimolar portions of 2-selenopyridine and 2-bromopyridine in boiling benzene in a nitrogen atmosphere. The precipitate which formed in the reaction mixture consisted of the dihydrobromide (4) of 3. 2,2'-Selenodipyridine (3) was obtained by evaporation of the benzene solution and a further quantity was forthcoming after neutralisation of 4. 2,2'-Selenodipyridine is a yellow oil.

Reaction of 2,2'-selenodipyridine (3) with boiling dibromomethane resulted in the formation of 6H-dipyrido[2,1-b:1',2'-e]-1,3,5-selenadiazinium dibromide (2). The structure was confirmed by elemental analyses (all bromine ionic) and by the NMR spectrum in water which consisted of a singlet at δ = 7.22 ppm assigned to the methylene protons at position 6, a multiplet at 8.10-8.80 due to the protons in positions 1, 2, 3, 9, 10, 11 and a doublet at 9.46-9.56 due to the protons in positions 4 and 8 with an integral area ratio of 1:3:1. The signal due to the methylene protons slowly diminished in intensity when the spectrum was run in D2O due to deuterium exchange. The salt 2 is a reactive compound and is readily broken down by alkali.

Experimental

Microanalyses, UV and NMR spectra were obtained as described previously. 

2,2'-Selenodipyridine (3)

2-Selenopyridine (6.4 g) and 2-bromopyridine (6.4 g) were refluxed in benzene (25 ml) for 2.5 h in an atmosphere of nitrogen. The yellow-orange precipitate (7.1 g) was filtered off and crystallised twice from methanol containing a little water to afford the dihydrobromide (4) of 2,2'-selenodipyridine as yellow crystals of the hemihydrate, m.p. 224-226 °C (decomp.).

C16H10Br2NaSe • 1/2 H2O
Calcd C 29.6 H 2.7 N 6.9,
Found C 29.3 H 2.4 N 6.6.

Evaporation of the benzene solution afforded an oil (5.15 g), which on distillation afforded 2,2'-selenodipyridine as a yellow oil, b.p. 135-140 °C/0.5 mm.

C16H9NaSe
Calcd C 51.1 H 3.4 N 11.9,
Found C 50.8 H 3.3 N 11.8.

UV spectrum (C6H6OH): λmax 246, 289, (log ε 3.80, 3.77) [nm].

Neutralisation of the solid dihydrobromide (4) with aqueous potassium carbonate afforded a further quantity of 2,2'-selenodipyridine. The total yield of 3 was 80%.

6H-Dipyrido[2,1-b:1',2'-e]-1,3,5-selenadiazinium Dibromide (2)

2,2'-Selenodipyridine (2.5 g) was refluxed with dibromomethane (18 ml) for 8 h in an atmosphere of nitrogen. The brown solid which was obtained was digested in methanol to give a yellow solid. This solid was crystallised from methanol with a trace

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of water to give yellow crystals of the hemihydrate, m.p. 263–264 °C (decomp.). Yield (65%).

C\textsubscript{11}H\textsubscript{16}Br\textsubscript{2}N\textsubscript{2}Se
Calcd  C 31.6  H 2.65  N 6.7  Br 38.2.
Found  C 31.6  H 2.6  N 7.0  Br (total) 37.8.

NMR spectrum (H\textsubscript{2}O): δ = 7.22 (s, 2H, CH\textsubscript{2}); 8.10–8.80 (m, 6H, protons at 1, 2, 3, 9, 10, 11); 9.46–9.56 (d, 2H, protons at 4, 8) [ppm].

UV spectrum (dilute aqueous HBr): λ\textsubscript{max}; 233, 277, 377 (log ε 4.22, 4.04, 3.58) [nm].

3 L. A. SUMMERS, Tetrahedron 24, 2697 [1968].