Selenium Heterocycles; Part I. Synthesis of 2,3-Dihydroselenolo[2,3-*b*]quinolines

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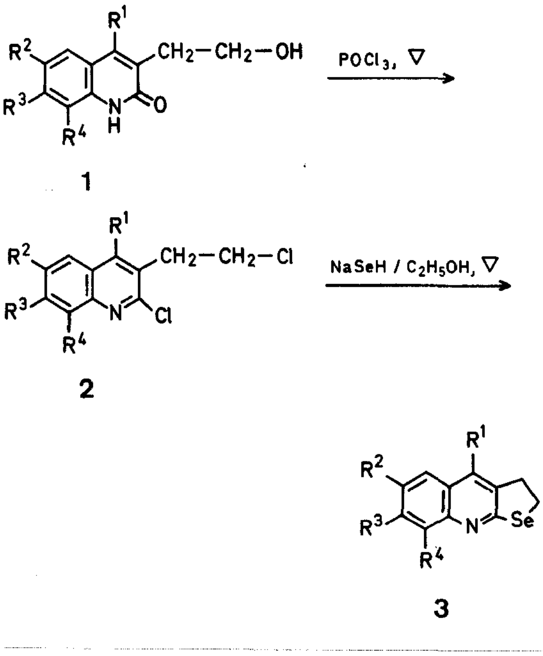
Selenolo[2,3-*b*]quinoline is a hitherto unreported heterocycle though its oxygen and sulfur analogs are available through several routes[1]. It was felt that a 2-oxoquinoline with appropriate substitution in the 3-position would serve as a precursor to this system. In this communication we wish to report a facile synthesis of the title heterocycles using 3-(2-hydroxyethyl)-2-oxoquinolines (**1**). Heating 2-chloro-3-(2-chloroethyl)-4-methylquinoline (**2a**)[2] with an ethanolic solution of sodium hydroselenide prepared *in situ*[3a, 3b] afforded a base on workup. This was identified as **3a** on the basis of its microanalysis, mass spectrum ($m/e=248$), and ^{1}H-N.M.R. spectrum, which closely resembled that of 4-methyl-2,3-dihydrothieno[2,3-*b*]quinoline[4]. A similar sequence, when extended to the hydroxyethyl-2-oxoquinolines (**1b**–**1d**), furnished the corresponding dihydroselenolo[2,3-*b*]quinolines (**3b–3d**) in fair to good yields. In the ^{1}H-N.M.R. spectra of these dihydroselenolo compounds, the C-2- and C-3-methylene protons were superimposed and appear as an unresolved four-proton singlet.



Compound	R^1	R^2	R^3	R^4
a	CH_3	H	H	H
b	H	CH_3	H	H
c	CH_3	H	H	OCH_3
d	H	H	H	H

Melting points were determined on a Boetius microheating table and are uncorrected. The N.M.R. spectra were determined on a Varian A-60 Spectrometer (TMS as internal standard).

2-Chloro-3-(2-chloroethyl)-quinolines (2):

The dichlorocompounds were obtained by a similar procedure employed for the preparation of **2a**[2] from **1a**. Use of **1b**[5], **1c**[6a], and **1d**[6b] led respectively to **2b**, **2c**, and **2d**. (For yield, m.p., etc. see Table 1).

Table 1. 2-Chloro-3-(2-chloroethyl)-quinolines (**2a–d**)

Compound	m.p.	Yield[a] [%]	Empirical Formula[b]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
2a	134–136°	68	$C_{12}H_{11}Cl_2N$ (240.1)	2.78, (s, 3H, $C\underline{H}_3$), 3.3–3.98 (m, 4H, $C\underline{H}_2$—$C\underline{H}_2$—Cl), 7.55–8.2 (m, 4H, $\underline{H}$—C-5, -6, -7, and -8)
2b	92–93°	96	$C_{12}H_{11}Cl_2N$ (240.1)	2.57 (s, 3H, $C\underline{H}_3$), 3.36+3.93 (t, 4H, $C\underline{H}_2$—$C\underline{H}_2$—Cl, $J=7$ Hz), 7.33–7.97 (m, 4H, $\underline{H}$—C-4, -5, -7, and -8)
2c	142–143°	71	$C_{13}H_{13}Cl_2NO$ (270.1)	2.73 (s, 3H, $C\underline{H}_3$), 3.27–3.97 (m, 4H, $C\underline{H}_2$—$C\underline{H}_2$—Cl), 4.23 (s, 3H, $OC\underline{H}_3$), 7.05–7.73 (m, 3H, H—C-5, -6, and -7)
2d	63–64°	65	$C_{11}H_9Cl_2N$ (226.1)	3.33+3.9 (t, 4H, $C\underline{H}_2$—$C\underline{H}_2$—Cl, $J=7$ Hz), 7.5–8.25 (m, 5H, H—C-4, -5, -6, -7, and -8)

[a] Recrystallised from benzene/petrol ether (60–80°).

[b] All products gave satisfactory microanalyses (C ±0.12%, H ±0.10%, N ±0.22%).

Table 2. 2,3-Dihydroselenolo[2,3-*b*]quinolines (**3a–d**)

Compound	m.p.	Yield[a] [%]	Empirical Formula[b]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
3a	153–154°	69	$C_{12}H_{11}NSe$ (248.2)	2.50 (s, 3H, $C\underline{H}_3$), 3.46 (s, 4H, $C\underline{H}_2$—$C\underline{H}_2$), 7.45–8.01 (m, 4H, $\underline{H}$—C-5, -6, -7, and -8)
3b	88–89°	75	$C_{12}H_{11}NSe$ (248.2)	2.47 (s, 3H, $C\underline{H}_3$), 3.47 (s, 4H, $C\underline{H}_2$—$C\underline{H}_2$), 7.3–7.93 (m, 4H, $\underline{H}$—C-4, -5, -7, and -8)
3c	193–194°	82	$C_{13}H_{13}NOSe$ (278.2)	2.5 (s, 3H, $C\underline{H}_3$), 3.47 (s, 4H, $C\underline{H}_2$—$C\underline{H}_2$), 4.07 (s, 3H, OCH_3), 6.83–7.53 (m, 3H, $\underline{H}$—C-5, -6, and -7)
3d	113–115°	65	$C_{11}H_9NSe$ (234.2)	3.5 (s, 4H, $C\underline{H}_2$—$C\underline{H}_2$), 7.42–8.16 (m, 5H, $\underline{H}$—C-4, -5, -6, -7, and -8)

[a] Recrystallised from benzene/petrol ether (60–80°).

[b] All products gave satisfactory microanalyses (C ±0.06%, H ±0.08%, N ±0.17%).

2,3-Dihydroselenolo[2,3-*b*]quinolines (3):

To a solution of sodium hydroselenide[3a, b], freshly prepared from selenium (0.80 g) and sodium borohydride (0.50 g) in ethanol was added **2a** (1.8 g, 8 mmol). The mixture was then heated at reflux on a steam bath for 5 h. Thereafter the solution was evaporated and the residue was taken up in chloroform and partitioned with water. The organic extract, after drying (Na_2SO_4), was evaporated. Chromatography of the residue over alumina with benzene furnished **3a** as pale yellow crystals: yield: 1.24 g (69%): m.p. 153–154°.

The selenoloquinolines **3b–3d** were obtained from the respective dichloro-compounds **2b–2d** by a similar procedure as described for **3a**. (For yield, m.p., etc. see Table 2.) The analytical samples were prepared by recrystallisation from benzene/petrol ether (60–80°).

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