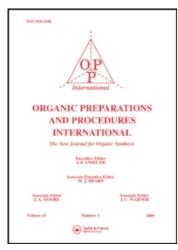
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THIENOQUINOLINES. PART V. AN IMPROVED SYNTHESIS OF 2,3-DIHYDROTHIENO[2,3-b]QUINOLINE AND ITS DERIVATIVES

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One of the methods 1-5 for the preparation of the thieno[2,3-b]quinoline system is based on 3-(2'-hydroxyethyl)-2-quinoline (<u>la</u>) as the starting point. la 2,3-Dihydrothieno[2,3-b]quinoline (<u>2a</u>) was obtained from <u>la</u> by the three-step sequence shown below.

This method was not extended to derivatives of <u>la</u>. The ready availability of several 3-(2'-hydroxyethyl)-2-quinolines through our recently reported method 6,7 prompted us to explore this route for the synthesis of the title compounds. However, the yield realized by Kuwayama in the conversion of <u>la</u> to <u>2a</u> by the above sequence is rather poor (25%). This communication reports a facile and one-step procedure for the conversion of <u>la</u> and its derivatives into the corresponding dihydrothienoquinolines. A pyridine solution of <u>la</u>, when heated with P_2S_5 furnished <u>2a</u> in 80% yield. Extension of this transformation to <u>lb</u> - <u>li</u> gave the respective hitherto unknown dihydrothieno[2,3-b]quinolines (<u>2b</u> - <u>2i</u>) in fair to good yield (51 - 100%). This procedure is operatively very simple and convenient.

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$$R_{1}^{2} \xrightarrow{R_{1}^{1}} CH_{2}CH_{2}OH \xrightarrow{Pyridine} R^{2} \xrightarrow{R^{1}} X$$
a) $R^{1} = R^{2} = R^{3} = R^{4} = H$
b) $R^{1} = R^{3} = R^{4} = H$, $R^{2} = OCH_{3}$
c) $R^{1} = R^{3} = R^{4} = H$, $R^{2} = CH_{3}$
d) $R^{1} = R^{3} = R^{4} = H$, $R^{2} = C1$
e) $R^{1} = R^{3} = R^{4} = H$, $R^{2} = C1$
i) $R^{1} = R^{2} = H$, $R^{3} = C1$, $R^{4} = CH_{3}$
e) $R^{1} = R^{4} = OCH_{3}$, $R^{2} = R^{3} = H$

TABLE I.- 2,3-Dihydrothieno[2,3-b]quinolines

Compound	Yield (%)	mp (°C)	Elemental Analysis % calculated (% found)	
			C	H
<u>2a</u>	80	104-105 ^a (lit. ^{la} , mp 104-106)	70.53 (70.50)	4.84 (4.89)
<u>2b</u>	62	144-145 ^a	66.31 (66.22)	5.10 (5.18)
<u>2c</u>	69	107 - 108 ^b	71.60 (71.49)	5.51 (5.64)
<u>2đ</u>	100	163 - 165 ^e	59.58 (59.72)	3.64 (3.71)
<u>2e</u>	51	108 - 109 ^b	63.13 (63.40)	5.30 (5.42)
<u>2f</u>	63	106-108 ^a	72.51 (72.46)	6.09 (6.06)
<u>2g</u>	61	139-140 ^a	57.25 (57.41)	4.00 (4.13)
<u>2h</u>	79	107 - 108 ^a	61.13 (61.64)	4.28 (4.64)
<u>2i</u>	62	139-140 ^a	61.13 (61.18)	4.28 (4.67)

From a: \underline{n} -hexane; b: benzene/ \underline{n} -hexane and c: benzene.

2,3-DIHYDROTHIENO[2,3-b]QUINOLINE AND ITS DERIVATIVES

TABLE II.- Proton nmr Spectra* of 2,3-dihydrothieno[2,3-b]quinolines.

Compound	-S-CH ₂ -CH ₂	С ₄ -Н	Aromatic Protons	OCH ₃ or CH ₃
<u>2a</u>	3.43		7.30 - 8.03 (m,5H)	
<u>2b</u>	3.37	7.60	6.90(d,1H,C ₅ -H,J=2.5Hz) 7.23(dd,1H,C ₇ -H,J=9,2.5Hz) 7.77(d,1H,C ₈ -H,J=9Hz)	3.83 (OCH ₃)
<u>2e</u>	3.40	7.60	7.30-7.53(m,2H, C_5 -H) and C_7 -H) 7.80(d,1H, C_8 -H,J=9Hz)	2.47 (CH ₃)
<u>2d</u>	3.40	7.53	7.33-7.53(m,2H, C_5 -H and C_7 -H) 7.80(d,1H, C_8 -H, J =9Hz)	
<u>2e</u>	3.40	8.13	6.60(d,1H,C ₆ -H or C ₇ -H,J=8Hz) 6.87(d,1H,C ₆ -H or C ₇ -H,J=8Hz)	3.90,4.0 (OCH ₃)
<u>2f</u>	3.40	7.87	7.07(d,1H,C ₆ -H or C ₇ -H,J=8Hz) 7.30(d,1H,C ₆ -H or C ₇ -H,J-8Hz)	2.70,2.53 (CH ₃ , CH ₃)
<u>2g</u>	3.50	8.13	6.87(d,lH,C ₇ -H,J=9Hz) 7.37(d,lH,C ₆ -H,J=9Hz)	4.03 (OCH ₃)
<u>2h</u>	3.47	8.13	7.33(s,2H, c_6 -H and c_7 -H)	2.67 (CH ₃)
<u>2i</u>	3.40	7.63	7.33(s,2H, C_5 -H and C_6 -H)	2.77 (CH ₃)

^{*}Spectra were recorded in CDCl $_3$ solution on a Varian T-60 instrument. Chemical shifts are expressed in δ (ppm) values with TMS as internal standard. The integrations of signals are consistent with their assignments. s = singlet; m = multiplet; d = doublet and dd = doublet of doublet.

EXPERIMENTAL

General Procedure. A mixture of the quinolonyl ethanol ($\underline{1}$) (200-400 mg), phosphorus pentasulfide (400-800 mg) and dry pyridine (20-25 ml) was heat-

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ed at reflux for 4 to 6 hr. It was evaporated under diminished pressure to give a residue which was dissolved in conc. hydrochloric acid (20 ml) and partitioned with benzene (3 x 20 ml portions). The base was recovered from the aqueous solution by basification with $^{40}\%$ sodium hydroxide followed by extraction with chloroform (3 x 50 ml portions). The chloroform extract after washing with water was dried ($^{82}\text{SO}_{4}$) and evaporated. The crystalline product was recrystallized from a suitable solvent.

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