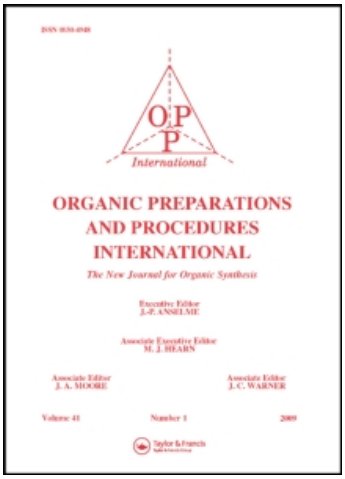

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THIENOQUINOLINES. PART V. AN IMPROVED SYNTHESIS OF 2,3-DIHYDROTHIENO[2,3-b]QUINOLINE AND ITS DERIVATIVES

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

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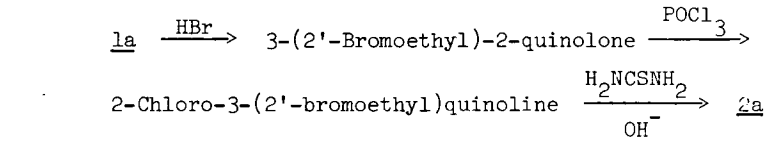
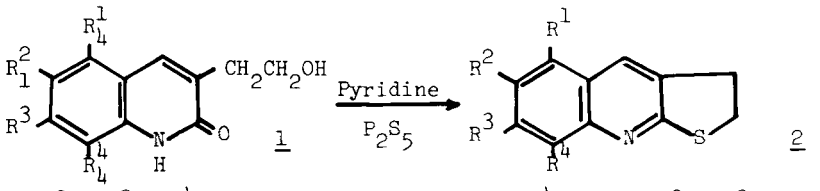
One of the methods[1-5] for the preparation of the thieno[2,3-b]quinoline system is based on 3-(2'-hydroxyethyl)-2-quinoline (1a) as the starting point.[1a] 2,3-Dihydrothieno[2,3-b]quinoline (2a) was obtained from 1a by the three-step sequence shown below.



This method was not extended to derivatives of 1a. The ready availability of several 3-(2'-hydroxyethyl)-2-quinolines[6] 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 1a to 2a by the above sequence is rather poor (25%). This communication reports a facile and one-step procedure for the conversion of 1a and its derivatives into the corresponding dihydrothienoquinolines. A pyridine solution of 1a, when heated with P_2S_5 furnished 2a in 80% yield. Extension of this transformation to 1b - 1i gave the respective hitherto unknown dihydrothieno[2,3-b]quinolines (2b - 2i) in fair to good yield (51 - 100%). This procedure is operatively very simple and convenient.



1 2

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) $R^1 = R^3 = R^4 = H$, $R^2 = Cl$

e) $R^1 = R^4 = OCH_3$, $R^2 = R^3 = H$

f) $R^1 = R^4 = CH_3$, $R^2 = R^3 = H$

g) $R^1 = Cl$, $R^2 = R^3 = H$, $R^4 = OCH_3$

h) $R^1 = Cl$, $R^2 = R^3 = H$, $R^4 = CH_3$

i) $R^1 = R^2 = H$, $R^3 = Cl$, $R^4 = CH_3$

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

Compound	Yield (%)	mp (°C)	Elemental Analysis % calculated (% found) C	H
2a	80	104-105[a] (lit.[1a], mp 104-106)	70.53 (70.50)	4.84 (4.89)
2b	62	144-145[a]	66.31 (66.22)	5.10 (5.18)
2c	69	107-108[b]	71.60 (71.49)	5.51 (5.64)
2d	100	163-165[c]	59.58 (59.72)	3.64 (3.71)
2e	51	108-109[b]	63.13 (63.40)	5.30 (5.42)
2f	63	106-108[a]	72.51 (72.46)	6.09 (6.06)
2g	61	139-140[a]	57.25 (57.41)	4.00 (4.13)
2h	79	107-108[a]	61.13 (61.64)	4.28 (4.64)
2i	62	139-140[a]	61.13 (61.18)	4.28 (4.67)

From a: n-hexane; b: benzene/n-hexane and c: benzene.

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

Compound	$-S-CH_2-CH_2$ (s)	C_4-H	Aromatic Protons	OCH_3 or CH_3 (s)
2a	3.43		7.30 - 8.03 (m,5H)	--
2b	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)
2c	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)
2d	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)	--
2e	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) (OCH_3)
2f	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)
2g	3.50	8.13	6.87(d,1H,C_7-H,J=9Hz) 7.37(d,1H,C_6-H,J=9Hz)	4.03 (OCH_3)
2h	3.47	8.13	7.33(s,2H,C_6-H and C_7-H)	2.67 (CH_3)
2i	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 (1) (200-400 mg), phosphorus pentasulfide (400-800 mg) and dry pyridine (20-25 ml) was heat-

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 (Na_2SO_4) and evaporated. The crystalline product was recrystallized from a suitable solvent.

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REFERENCES

† Part IV. P. Shanmugam, K. Kanakarajan, and N. Soundararajan, Z. Naturforsh. (1976) (Submitted).

1. a) Y. Kuwayama, Yakugaku Zasshi, 82, 1028 (1962), Chem. Abs., 58 5687 (1963).

   b) G. Kobayashi, Y. Kuwayama, and S. O. Kamura, ibid., 82, 234 (1963), Chem. Abs., 59, 5144 (1963).

2. T. Jen, B. Dienel, F. Dowalo, H. Van Hoeven, P. Bender, and B. Loev, J. Med. Chem. 16, 633 (1973).

3. R. Hull, J. Chem. Soc. Perkin I, 2911 (1973).

4. P. Shanmugam, K. Kanakarajan, N. Soundararajan, and A. Gnanasekaran, Synthesis, 253 (1976).

5. P. Shanmugam, K. Kanakarajan, and N. Soundararajan, Z. Naturforsch. (1976). In Press.

6. P. Shanmugam, T. K. Thiruvengadam, and R. Palaniappan, Z. Naturforsch. (b) 28, 551 (1973).

7. P. Shanmugam, T. K. Thiruvengadam, and K. Ramasamy, Monatsh, Chem. (1976) (Submitted).

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