

## Thienoquinolines. Part 6.<sup>1</sup> Reaction of 2-Chloro-3-(1,2-Dibromoethyl)-quinolines with Thiourea: a Convenient Synthesis of Thieno[2,3-*b*]-quinolines

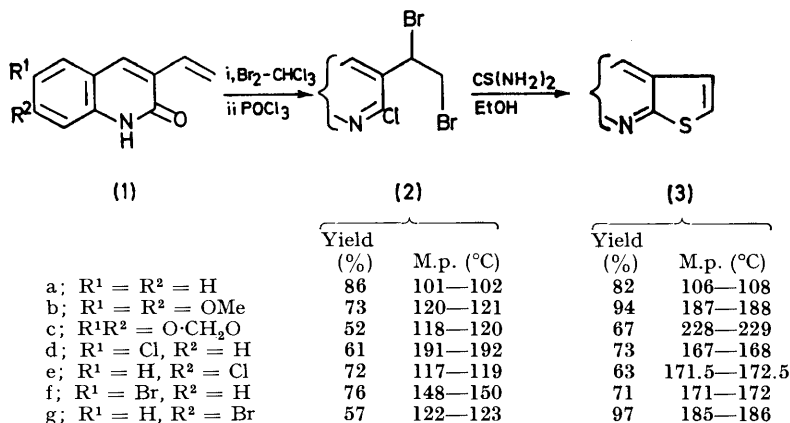
By Periappa Shanmugam,\* Nachimuthu Soundararajan, and Kuppusamy Kanakarajan, Department of Chemistry, Madras University Post-graduate Centre, Coimbatore 641004, Tamil Nadu, India

The reactions of 2-chloro-3-(1,2-dibromoethyl)quinolines (2) with thiourea in protic solvents affords thieno[2,3-*b*]quinolines (3) in high yields.

We have previously described<sup>2</sup> the synthesis of several thieno[2,3-*b*]quinolines from 3-vinylquinolin-2(1*H*)-ones. This method was applicable only in the 4-substituted series. Attempts to prepare the parent thienoquinoline (3a) and its 4-unsubstituted derivatives were unsuccessful because of our inability to obtain the corresponding 2-chloro-3-vinylquinolines, required as intermediates. In an alternative approach, we saturated the vinyl group of the quinolone (1a)<sup>3</sup> with bromine and treated the resulting dibromide with phosphoryl chloride to yield 2-chloro-3-(1,2-dibromoethyl)quinoline (2a).

Spectral and analytical data for all new compounds are available as Supplementary Publication No. SUP 22097 (5 pp.).†

**2-Chloro-3-(1,2-dibromoethyl)quinolines (2a—g).**—To a cooled (0—5 °C), stirred suspension of the appropriate 3-vinylquinolin-2(1*H*)-one (1a—g) (10 mmol) in anhydrous chloroform (50 ml) was added dropwise a solution (20 ml) of bromine (11 mmol) in chloroform during 30 min. Stirring and cooling were continued for a further 45 min. To the stirred mixture, light petroleum (b.p. 40—60 °C) was added in excess, and the mixture was allowed to attain room temperature. The pale yellow powder that separated



When the product (2a) was boiled with a stoichiometric amount (or more) of thiourea in ethanol, it gave the parent thienoquinoline (3a), identical with authentic material derived from methyl thieno[2,3-*b*]quinoline-4-carboxylate.<sup>4</sup> Use of other protic solvents (methanol, propanol, or aqueous acetone) in place of ethanol, led to the same result. However when the reaction was repeated in aprotic solvents (dry benzene, dry chloroform, or dry acetone) the trihalogeno-compound was unchanged.

Similarly the vinylquinolones (1b—g)<sup>3,5</sup> furnished the thienoquinolines (3b—g) in high yield.

### EXPERIMENTAL

General experimental details were as reported previously.<sup>2</sup> Light petroleum refers to the fraction of b.p. 60—80 °C unless stated otherwise.

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1976, Index issue.

<sup>1</sup> Part 5, P. Shanmugam, T. K. Thiruvengadam, and N. Soundararajan, *Org. Prep. Proced. Int.*, 1976, **8**, 279.

<sup>2</sup> P. Shanmugam, K. Kanakarajan, N. Soundararajan, and A. Gnanasekaran, *Synthesis*, 1976, 253.

was collected, washed with dry ether, and dried *in vacuo*. This adduct was heated with freshly distilled phosphoryl chloride (5 ml) on a steam-bath for 4 h. The product was cooled and poured onto crushed ice, and the white solid which separated was collected, washed with ice-water, and dried. Purification was effected by dissolving the solid in dry benzene and filtering through a small bed of basic alumina in a sintered crucible. The filtrate was evaporated and the residue was recrystallised from benzene-light petroleum.

**Thieno[2,3-*b*]quinolines (3a—g).**—A solution of compound (2) (2 mmol) and thiourea (2 mmol) in dry ethanol (20 ml) was heated at reflux for 5 h. The solvent was then allowed to boil off and the residue was taken up in chloroform and partitioned with water. The chloroform extracts were combined, washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. Chromatography of the residue over alumina in benzene followed by recrystallisation furnished the product (3).

<sup>3</sup> P. Shanmugam and R. Palaniappan, *Z. Naturforsch.*, 1973, **28b**, 196.

<sup>4</sup> P. Shanmugam, K. Kanakarajan, and N. Soundararajan, *Z. Naturforsch.*, 1976, **31b**, 1297.

<sup>5</sup> P. Shanmugam, R. Palaniappan, N. Soundararajan, T. K. Thiruvengadam, and K. Kanakarajan, *Monatsh.*, 1976, **107**, 259.

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