

during this time. The n.m.r. spectrum of an aqueous solution of (7a) showed no change after 1 day. Since deuteration occurs under these conditions, and since the intermediate carbanion must be reprotonated to give the thermodynamically more stable product, the product isolated must have the thermodynamically more stable configuration. Both the *cis*- and the *trans*-isomers apparently can assume cyclohexane conformations which fit the observed coupling constant for the dihydrothiazole ring protons. Application of the suggested *cis*-addition mechanism (Scheme 1), however, leads to the assignment of the *cis*-configuration to the product, since it has been established that cyclisation in related compounds proceeds with configurational inversion (Scheme 2).⁸ The question of relative stereochemistry was unambiguously solved for compound (7d) by X-ray analysis, and the *cis*-configuration was confirmed.⁹ All the members of the series must have the same configuration since the coupling constants for the vicinal dihydrothiazole protons are almost the same.

The X-ray analysis⁹ shows that the five-membered ring has the envelope conformation with C-2 0.60 Å out of the plane of the other four dihydrothiazole ring atoms. A similar envelope conformation has been seen in a *trans*-2,3-dicarboxy-analogue (C-2 0.57 Å out of plane⁴). The cyclohexanone ring has the chair conformation. The 2,3-torsion angle ($41 \pm 3^\circ$) is larger than expected^{6,7} on the basis of the coupling constant (7.0 Hz) in CF₃·CO₂H solution.

EXPERIMENTAL

N.m.r. spectra were recorded for solutions in trifluoroacetic acid with a Varian A-60A instrument and u.v. spectra were obtained with a Perkin-Elmer 137-UV instrument.

4b,10a-Dihydro-9-methyl-11-oxoindeno[2',1'-4,5]thiazolo[3,2-a]pyridinium Bromide (4).—2,3-Dibromoindanone⁵ (1.16 g, 0.004 mol) was dissolved in ethyl acetate (30 ml) and diethylamine (0.29 g, 0.004 mol) was added. An immediate exothermic reaction ensued with precipitation of diethylamine hydrobromide. The precipitate was filtered off after 10 min under anhydrous conditions. The filtrate containing the generated 2-bromoindanone was then

⁸ K. Undheim and G. A. Ulsaker, *Acta Chem. Scand.*, in the press.

added dropwise to a solution of 6-methylpyridine-2-thione (0.50 g, 0.004 mol) in ethyl acetate (40 ml). The precipitate was collected after 1 day in the cold (0.60 g, 45%) and recrystallised from ethanol; m.p. 246–248 °C (decomp.) (Found: C, 53.7; H, 3.8; N, 4.05. C₁₅H₁₂BrNOS requires C, 53.9; H, 3.6; N, 4.2%), τ 3.47 (4b-H), 3.18 (10a-H) (*J* 8.0 Hz), 6.80 (Me), and 1.6–2.4 (aromatic), λ_{\max} (0.1N-HCl) 330 (log ϵ 3.50) and 245sh nm (4.0).

5a,6,7,8,9,9a-Hexahydro-9-oxopyrido[2,1-b]benzothiazolium Bromide and Derivatives (7).—A solution of 2-bromocyclohex-2-enone¹⁰ (0.83 g, 0.0047 mol) in chloroform (30 ml) was added dropwise to a chloroform solution (50 ml) of a pyridine-2-thione (1) (0.005 mol). The chloroform was distilled off when the reaction was complete [1 day for (7a, b, and d), 3 days for (7c)] and the residual oil was dissolved in ethanol-acetone, from which the desired substance slowly crystallised out. Yellowish-white crystals were obtained on recrystallisation from acetone to which had been added a drop of hydrobromic acid.

Compound (7a) (71%) had m.p. 155–156 °C (decomp.) (Found: C, 45.9; H, 4.45; N, 5.1. C₁₁H₁₂BrNOS requires C, 46.15; H, 4.2; N, 4.9%), τ 4.6 (5a-H), 3.73 (9a-H) (*J* 7.5 Hz), 1.2–2.4 (pyridine H), and 7.1–8.0 (cyclohexane H), λ_{\max} (0.1N-HCl) 330 (log ϵ 3.74), 240 (3.92), and 213 nm (3.85).

The 1-methyl derivative (7b) (65%) had m.p. 248–249 °C (decomp.) (Found: C, 47.75; H, 4.55; N, 4.7. C₁₃H₁₄BrNOS requires C, 48.0; H, 4.7; N, 4.65%), τ 4.6 (5a-H), 3.62 (9a-H) (*J* 7.0 Hz), 7.22 (Me), 1.6–2.5 (pyridine H), and 6.9–7.8 (cyclohexane H), λ_{\max} (0.1N-HCl) 331 (log ϵ 3.81), 240 (3.88), and 211 nm (3.88).

The 4-hydroxy-1-methyl derivative (7c) (78%) had m.p. 243–244 °C (decomp.) (Found: C, 45.35; H, 4.55; N, 4.5. C₁₃H₁₄BrNO₂S requires C, 45.6; H, 4.45; N, 4.45%), τ 4.7 (5a-H), 3.70 (9a-H) (*J* 7.0 Hz), 7.35 (Me), 2.60 (2-H), 2.15 (3-H), and 7.0–7.8 (cyclohexane H), λ_{\max} (0.1N-HCl) 348 (log ϵ 4.00), 241 (3.92), and 216 nm (4.11).

The 4-ethoxy-1-methyl derivative (7d) (80%) had m.p. 198–199 °C (decomp.) (Found: C, 48.6; H, 5.3; N, 4.1. C₁₄H₁₈BrNO₂S requires C, 48.85; H, 5.3; N, 4.05%), τ 4.7 (5a-H), 3.80 (9a-H) (*J* 7.0 Hz), 7.33 (Me), 2.53 (2-H), 2.28 (3-H), 6.9–7.9 (cyclohexane H), and 5.63 and 8.45 (OEt), λ_{\max} (0.1N-HCl) 349 (log ϵ 3.95), 243 (3.91), and 218 nm (3.94).

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⁹ P. Groth, *Acta Chem. Scand.*, 1972, **26**, 3131.

¹⁰ F. G. Bouvell and K. M. Wellman, *J. Org. Chem.*, 1963, **28**, 2544.