# Some Polycyclic Systems related to [1]Benzothieno[2,3-*c*]pyridine

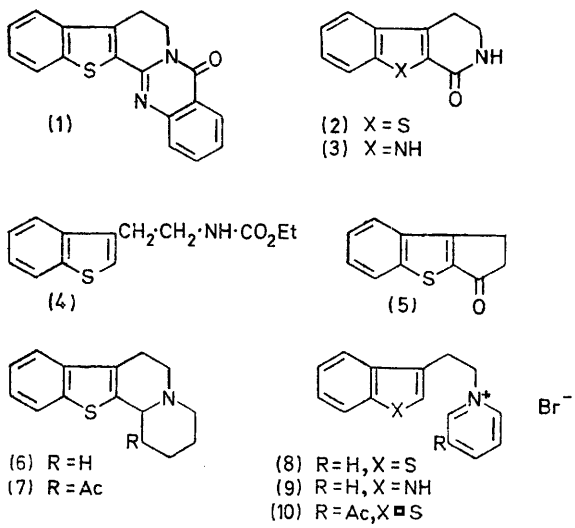
By **N. B. Chapman,* C. G. Hughes,** and **R. M. Scrowston,** Department of Chemistry, The University, Hull HU6 7RX

3,4-Dihydro[1]benzothieno[2,3-*c*]pyridin-1(2*H*)-one (2) has been prepared by Bischler–Napieralski cyclisation of *N*-ethoxycarbonyl-2-(3-benzo[*b*]thienyl)ethylamine (4) and by Beckmann rearrangement of the mixture of stereoisomeric oximes from 1,2-dihydrocyclopenta[*b*][1]benzothiophen-3-one (5). It condensed with methyl anthranilate to give the sulphur analogue (1) of rutecarpine.

Oxidation of *N*-2-(3-benzo[*b*]thienyl)ethylpiperidine (13) with mercury(II) acetate gave a tetracyclic product (6); a related compound (7) was obtained by partial catalytic reduction of 3-acetyl-*N*-2-(3-benzo[*b*]thienyl)-ethylpyridinium bromide (10) and treatment of the resulting 5-acetyl-*N*-2-(3-benzo[*b*]thienyl)ethyl-1,2,3,4-tetrahydropyridine (15) with hydrochloric acid. Reduction ($LiAlH_4$) of *N*-2-(3-benzo[*b*]thienyl)ethylpyridinium bromide (8) took place only in the pyridine ring, and did not lead to tetracyclic products.

CURRENT interest [1-3] in the synthesis and biological properties of the sulphur analogues of indole alkaloids has led us to extend studies from this laboratory [4] on the benzo[*b*]thiophen analogues of β- and γ-carbolines and related compounds to include the preparation of the benzo[*b*]thiophen analogue (1) of rutecarpine.[5]

β-(3-Benzo[*b*]thienyl)propionic acid served as a useful starting material for the key intermediate, 3,4-dihydro-[1]benzothieno[2,3-*c*]pyridin-1(2*H*)-one (2). Together with certain by-products, which are described in the Experimental section, the former was obtained [6] from 3-chloromethylbenzo[*b*]thiophen by a standard diethyl malonate synthesis, and converted successively into the corresponding methyl ester, hydrazide, and azide. The corresponding azide in the indole series underwent the Curtius rearrangement when heated in an inert solvent, and the resulting isocyanate readily gave the lactam (3) when treated *in situ* with hydrogen chloride.[7] However, a similar attempted rearrangement and cyclisation of β-(3-benzo[*b*]thienyl)propionyl azide gave a mixture of 2-(3-benzo[*b*]thienyl)ethylamine hydrochloride (12%), the *sym*-urea $\{(ArCH_2{\cdot}CH_2{\cdot}NH)_2CO$; Ar = 3-benzo[*b*]-thienyl} (53%), and β-(3-benzo[*b*]thienyl)propionamide (15%). The remaining tarry material contained no cyclised product (2). The nature of these products suggests that they were formed by reaction of the inter-




mediate isocyanate with water present in the reaction mixture. Because of the instability of the azide it was

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[3] B. C. Elmes and J. M. Swan, *Austral. J. Chem.*, 1969, **22**, 1963.
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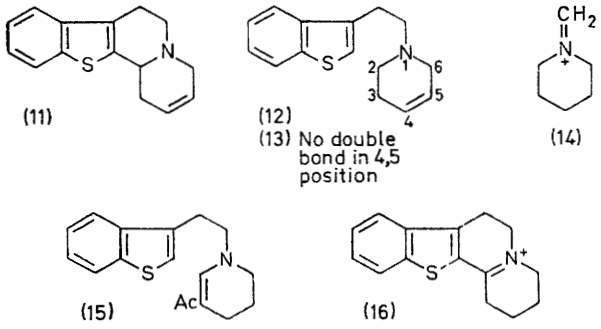
not possible to remove all traces of water, and similar products were obtained from several subsequent reactions. The isocyanate was therefore converted into the urethane (4), which was cyclised (61%) when treated with phosphoryl chloride and phosphorus pentoxide in a modified Bischler–Napieralski [8] reaction.

In another approach to the lactam (2), the mixture of stereoisomeric oximes (*ca.* 1 : 1) from 1,2-dihydrocyclopenta[*b*][1]benzothiophen-3-one (5) [6] was subjected to Beckmann rearrangement with polyphosphoric acid. The sole product was the required lactam (2), which suggests either that the *anti*-aryl oxime had isomerised to the *syn*-aryl configuration in the acidic medium,[9] or that Beckmann rearrangement had been non-stereospecific.[10] Finally, the intermediate (2) reacted with methyl anthranilate in the presence of phosphorus trichloride to give the sulphur isostere (1) of rutecarpine (43%).

Next we prepared the [1]benzothieno[2,3-*a*]quinolizines (6 and 7), which are useful model compounds for the synthesis of the sulphur analogues of certain more complex indole alkaloids, and which may themselves show interesting biological activity. First we reduced the pyridinium salt (8) with lithium aluminium hydride, in the hope that the expected [11] 1,2-dihydropyridine intermediate would give the tetracyclic compound (11) when treated with hydrochloric acid. However, the major product (85%) from the reaction was the tetrahydropyridine derivative (12). Its $^1$H n.m.r. spectrum showed the presence of two olefinic protons (δ 5·75 and 5·78 p.p.m.) and on catalytic hydrogenation (uptake 1 mol.) it gave *N*-2-(3-benzo[*b*]-thienyl)ethylpiperidine (13), which was prepared unambiguously by reduction ($LiAlH_4$) of *N*-(3-benzo[*b*]-thienyl)acetylpiperidine. The u.v. spectrum of the olefin (12) was very similar to that of the corresponding saturated compound (13), suggesting the location of the double bond in the 3,4-position of the piperidine ring. Structure (12) was confirmed by a multiplet at δ 2·85 (4H) (N·[$CH_2$]$_2$) and at δ 3·33 (2H) (N·$CH_2$·C:C) p.p.m. in the n.m.r. spectrum. The minor product (15%) from the reduction of the pyridinium salt (8) was not isolated, but it appears to be the piperidine derivative (13) (g.l.c.–mass spectrometry). The mass spectra of compounds of the type of (12) and (13) are very characteristic. The base peak [14 (from (13))] and a strong peak at *m/e* 147 (3-benzo[*b*]thenyl cation) are formed by cleavage β to the nitrogen atom. It is of interest that reduction ($LiAlH_4$) of the indole derivative (9) gives the olefin corresponding to (12), and very little cyclisation product.[12]

An alternative reductive procedure gave the tetracyclic compound (7) by catalytic hydrogenation (2 mol.) of the pyridinium salt (10), and treatment of the resulting tetrahydro-derivative (15) with hydrochloric acid (*cf.* Pictet–Spengler cyclisation [13]). Earlier experiments on related compounds in the indole series [14] had demonstrated the need to use the 3-acetylpyridinium salt in order to arrest the reduction at the crucial tetrahydro stage. The absence of vinylic proton signals from the n.m.r. spectrum of compound (7) confirmed that cyclisation had taken place.




Finally, *N*-2-(3-benzo[*b*]thienyl)ethylpiperidine (13) was oxidised with mercury(II) acetate [15] to give the tetracyclic product (6). A high yield (65%) was obtained only when the crude product was reduced with sodium borohydride. This procedure converts any of the quaternary salt (16) into the required product (6); such salts are common by-products of this type of reaction, and are formed by further oxidation of the initial product with mercury(II) acetate. The structure of the tetracyclic compound (6) was confirmed by its n.m.r. spectrum, which lacked a vinylic proton resonance, and by its mass spectrum, which was very similar to that of the indole analogue.[16]

## EXPERIMENTAL

I.r. spectra were determined for potassium chloride discs with a Unicam SP 200 spectrophotometer and u.v. spectra were obtained for solutions in 19 : 1 ethanol–water with a Unicam SP 700 spectrophotometer. $^1$H N.m.r. spectra were obtained with a JNM-4H-100 spectrometer (100 MHz), for solutions in deuteriochloroform with tetramethylsilane as internal standard. Molecular weights were obtained with an A.E.I. MS902 mass spectrometer. The purity of products was established wherever possible by t.l.c. on silica gel G (Merck). Light petroleum had b.p. 60—80°.

β-(3-*Benzo*[b]*thienyl*)*propionic Acid* (with Miss J. M. Willis).—(*a*) 3-Chloromethylbenzo[*b*]thiophen (42·5 g., 0·23 mole) was added during 1 hr. to a stirred, gently boiling solution of diethyl malonate (37 g., 0·23 mole) and sodium ethoxide [from sodium (5·5 g.)] in ethanol (150 ml.), and the resulting mixture was heated under reflux for 2 hr. The solvent was removed, water was added, and diethyl 3-benzo-[*b*]thenylmalonate was extracted with ether. Distillation

[8] W. M. Whaley and T. R. Govindachari, *Org. Reactions*, 1951, **6**, 74.
[9] *Cf.* A. P. Terent'ev and A. N. Makarova, *Vestnik Moskov. Univ.*, 1947, no. 4, 101 (*Chem. Abs.*, 1948, **42**, 1590).
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[13] W. M. Whaley and T. R. Govindachari, *Org. Reactions*, 1951, **6**, 151.
[14] E. Wenkert and B. Wickberg, *J. Amer. Chem. Soc.*, 1965, **87**, 1580.
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[16] G. Spiteller, *Adv. Heterocyclic Chem.*, 1966, **7**, 301.

gave a pale yellow oil (82%), b.p. 158—162°/0·2 mm. (lit.,[6] 230°/19 mm.), $\nu_{max.}$ 1735 cm.$^{-1}$ (C=O).

The crude ester (20 g.) was heated under reflux for 1·5 hr. with 50% aqueous potassium hydroxide. Some oily material remained, and was extracted with ether from the cooled mixture. Acidification of the aqueous solution gave 3-benzo[*b*]thenylmalonic acid, which was filtered off, dried, and heated at 230° until evolution of carbon dioxide had ceased (*ca.* 1·5 hr.). The brown residue was cooled and crystallised from benzene (charcoal) to give β-(3-benzo[*b*]-thienyl)propionic acid (40% overall from 3-chloromethyl-benzo[*b*]thiophen) as white needles, m.p. 143—145° (lit.,[6] 145°), $\nu_{max.}$ 1700 cm.$^{-1}$ (C=O).

(*b*) *Isolation of by-products.* The neutral oily material from the alkaline hydrolysis was heated under reflux with light petroleum. Insoluble material was filtered off and crystallised from ethanol to give 1,2-bis-(3-benzo[*b*]thienyl)-ethane as needles (0·2 g.), m.p. 139—141° (lit.,[17] 141·5—142·5°) (Found: *M*, 294. Calc. for $C_{18}H_{14}S_2$: *M*, 294). The cooled petroleum solution deposited white needles of *diethyl bis-(3-benzo*[b]*thenyl)malonate* (3·5 g.), m.p. 96—97° (from ethanol) (Found: C, 66·1; H, 5·4; S, 13·9%; *M*, 452. $C_{25}H_{24}O_4S_2$ requires C, 66·35; H, 5·35; S, 14·15%; *M*, 452), $\nu_{max.}$ ($CHCl_3$) 1705 cm.$^{-1}$, $\nu_{max.}$ (KCl) 1700 and 1735 cm.$^{-1}$ (C=O), δ 3·51 p.p.m. (s, $ArCH_2$). Alkaline hydrolysis of the diester in boiling diethylene glycol for 1·5 hr. gave the rather unstable *bis-(3-benzo*[b]*thenyl)malonic acid* (2·8 g.), m.p. 201° (decomp.) (white needles from ethyl acetate–light petroleum) (Found: C, 63·3; H, 4·1. $C_{21}H_{16}O_4S_2$ requires C, 63·6; H, 4·05%). Decarboxylation at 220° gave *bis-(3-benzo*[b]*thenyl)acetic acid* (1·8 g.), m.p. 166—167° (needles from ethyl acetate–light petroleum) (Found: C, 68·2; H, 4·6. $C_{20}H_{16}O_2S_2$ requires C, 68·15; H, 4·55%).

β-(3-*Benzo*[b]*thienyl)propionohydrazide* (with Miss J. M. Willis).—Methyl β-(3-benzo[*b*]thienyl)propionate (10·8 g., 0·05 mole) [obtained as an oil (98%) by treatment of a methanolic solution of the corresponding acid with ethereal diazomethane] and hydrazine hydrate (4 g.) were heated together under reflux for 2 hr. The hydrazide separated from the cooled solution as *needles* (9·1 g., 83%), m.p. 118—120° (from ethanol) (Found: C, 59·7; H, 5·4; N, 12·7%; *M*, 220. $C_{11}H_{12}N_2OS$ requires C, 59·95; H, 5·5; N, 12·7%; *M*, 220), $\nu_{max.}$ 1650 (C=O) and 1605 ($NH_2$) cm.$^{-1}$.

β-(3-*Benzo*[b]*thienyl)propionyl Azide.*—A concentrated aqueous solution of sodium nitrite (0·25 g.) was added to a vigorously stirred mixture of the hydrazide (0·5 g.), glacial acetic acid (2 ml.), 10% hydrochloric acid (10 ml.), toluene (20 ml.), and crushed ice (10 g.). After 5 min. the organic layer was separated, washed with aqueous sodium hydrogen carbonate, and dried thoroughly ($MgSO_4$). Because of its instability, the azide was used immediately without further purification.

*Curtius Rearrangement of* β-(3-*Benzo*[b]*thienyl)propionyl Azide.*—A solution of the azide in dry toluene was heated under reflux for 30 min., saturated with hydrogen chloride, and cooled. 2-(3-Benzo[*b*]thienyl)ethylamine hydrochloride (12%) was filtered off; it formed white needles, m.p. 217—219° (lit.,[18] 218—219°) (from ethanol–ether), identical (mixed m.p. and i.r. spectra) with authentic material. The filtrate was evaporated to dryness and the residue was chromatographed on alumina. Elution with chloroform gave NN′-*bis-2-(3-benzo*[b]*thienyl)ethylurea* (53%), m.p. 181—182° (white needles from chloroform) (Found: C, 65·9; H, 5·3; N, 7·4; S, 16·6%; *M*, 380. $C_{21}H_{20}N_2OS_2$ requires C, 66·3; H, 5·3; N, 7·35; S, 16·85%; *M*, 380), $\nu_{max.}$ 3360, 1580 (NH), and 1620 (C=O) cm.$^{-1}$. It was followed closely by β-(3-benzo[*b*]thienyl)propionamide (15%), which crystallised from benzene–light petroleum as needles, m.p. 96—98° (lit.,[6] 95°), $\nu_{max.}$ 1660 cm.$^{-1}$ (C=O), identical (mixed m.p. and i.r. spectra) with authentic material.

N-*Ethoxycarbonyl-2-(3-benzo*[b]*thienyl)ethylamine* (4).—A solution of β-(3-benzo[*b*]thienyl)propionyl azide (*ca.* 2 g.) in dry ether was treated with ethanol (100 ml.) and evaporated to dryness. The resulting pale yellow oil crystallised from light petroleum (b.p. 80—100°) to give the *urethane* (1·6 g., 70%) as white flakes, m.p. 33—35° (Found: C, 62·3; H, 6·0; N, 5·8; S, 12·9%; *M*, 249. $C_{13}H_{15}NO_2S$ requires C, 62·6; H, 6·05; N, 5·6; S, 12·85%; *M*, 249), $\nu_{max.}$ 3350 (NH) and 1700 (C=O) cm.$^{-1}$.

3,4-*Dihydro*[1]*benzothieno*[2,3-c]*pyridin-1*(2H)-*one* (2).—A mixture of the urethane (4) (0·5 g.), phosphorus pentoxide (1 g.), phosphoryl chloride (1 g.), and xylene (20 ml.) was heated under reflux for 1 hr. It was then poured into water and the organic layer was separated, washed, dried, and evaporated. The residue crystallised as silvery *plates* (0·25 g., 61%), m.p. 222—224° (from benzene) (Found: C, 65·0; H, 4·5; N, 6·7; S, 15·5%; *M*, 203. $C_{11}H_9NOS$ requires C, 65·0; H, 4·45; N, 6·9; S, 15·8%; *M*, 203), $\nu_{max.}$ 3300 (NH) and 1650 (C=O) cm.$^{-1}$

1,2-*Dihydrocyclopenta*[b][1]*benzothiophen-3-one* (5).—A stirred mixture of β-(3-benzo[*b*]thienyl)propionic acid (10 g., 0·05 mole) and polyphosphoric acid (150 g.) was kept for 1 hr. at 70—80°, then poured into water. The precipitate was collected, washed with aqueous sodium hydrogen carbonate [from which starting material (0·5 g.) was recovered], and crystallised from benzene (charcoal) to give the ketone (5) (6 g., 70%) as white needles, m.p. 148—150° (lit.,[6] 161°), $\nu_{max.}$ 1685 cm.$^{-1}$ (C=O). Cyclisation of the acid chloride [6,19] is less simple and gives a lower yield (60%).

The ketone formed a mixture of two stereoisomeric *oximes*, m.p. 202—204° (white needles from benzene) (Found: C, 64·8; H, 4·3; N, 7·0; S, 15·5%; *M*, 203. $C_{11}H_9NOS$ requires C, 65·0; H, 4·45; N, 6·9; S, 15·8%; *M*, 203), $\nu_{max.}$ 3200 (OH) and 1640 (C:N) cm.$^{-1}$. The mixture was separated by t.l.c. (in benzene); the components had similar mass spectra ($M^+$ 203).

*Beckmann Rearrangement of the Mixture of Oximes.*—The oximes just described (1 g.) were stirred with polyphosphoric acid (15 g.) for 20 min. at 125—130° and for 16 hr. at room temperature. Addition to water gave the lactam (2) (0·7 g., 70%), identical (mixed m.p. and i.r. spectra) with that prepared before.

*The Sulphur Isostere* (1) *of Rutecarpine.*—A mixture of 3,4-dihydro[1]benzothieno[2,3-*c*]pyridin-1(2*H*)-one (1·5 g.), methyl anthranilate (2 g.), phosphorus trichloride (8 g.), and dry xylene (20 ml) was heated under reflux for 15 hr., then poured into ice–water. The resulting precipitate crystallised from dimethylformamide–water as tan *needles* (0·8 g., 43%), m.p. 221—223° (Found: C, 70·6; H, 3·9; N, 8·9%; *M*, 304·0667. $C_{18}H_{12}N_2OS$ requires C, 71·0; H, 3·95; N, 9·2%; *M*, 304·0670), $\nu_{max.}$ 1675 cm.$^{-1}$ (C=O).

N-2-(3-*Benzo*[b]*thienyl)ethylpyridinium Bromide* (8).—3-(2-Bromoethyl)benzo[*b*]thiophen (12 g.) was prepared (47%) by the reaction of 3-(2-hydroxyethyl)benzo[*b*]thiophen [6] with phosphorus tribromide in dry chloroform. It

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[18] N. B. Chapman, K. Clarke, A. J. Humphries, and S. U-D. Saraf, *J. Chem. Soc.* (*C*), 1969, 1612.

[19] P. Cagniant and P. Cagniant, *Bull. Soc. chim. France*, 1953, 185.

had b.p. 124—127°/0·2 mm. (lit.,[6] 188°/21 mm.). A solution in pyridine (28 ml.) was heated under nitrogen for 8 hr. at 80°, cooled, and treated with dry acetone to precipitate the required salt. It formed *cubes* (12·8 g., 80%), m.p. 165—167° (from ethanol–ether) (Found: C, 55·9; H, 4·3; N, 4·0; S, 10·0. $C_{15}H_{14}BrNS$ requires C, 56·25; H, 4·4; N, 4·35; S, 10·0%).

N-2-(3-*Benzo*[b]*thienyl*)*ethylpiperidine* (13).—A solution of piperidine (40 ml.) in dry ethyl acetate (250 ml.) was added slowly to a cooled solution of 3-benzo[*b*]thienylacetyl chloride [from 3-benzo[*b*]thienylacetic acid [20] (19·2 g.)] in ethyl acetate (250 ml.) and the mixture was set aside for 4 hr. It was then washed successively with 2N-hydrochloric acid, aqueous sodium hydrogen carbonate, and water, dried, and evaporated.

The crude oily amide (21 g.) in dry ether (500 ml.) was added slowly to a stirred suspension of lithium aluminium hydride (10 g.) in ether (200 ml.), and stirring was continued for 5 hr. at room temperature. Basic material was isolated and distilled, to give the *amine* (16·3 g., 67%) as a yellow oil, b.p. 148—150°/0·2 mm. It solidified slowly to give white needles, m.p. 34—35° (from ether–light petroleum) (Found: C, 73·4; H, 7·6; N, 5·65%; *M*, 245. $C_{15}H_{19}NS$ requires C, 73·4; H, 7·8; N, 5·7%; *M*, 245), $\lambda_{max.}$ 230 (ε 29,000), 263 (4600), 270infl (4300), 291 (3000), and 300 (3500) nm. The *hydrochloride* formed needles, m.p. 280—282° (from ethanol–ether) (Found: C, 63·7; H, 7·2; N, 4·9; S, 11·2. $C_{15}H_{20}ClNS$ requires C, 63·9; H, 7·15; N, 4·95; S, 11·4%), $\nu_{max.}$ 2510 cm.$^{-1}$ ($NH^+$).

*Reduction of* N-2-(3-*Benzo*[b]*thienyl*)*ethylpyridinium Bromide* (8).—A suspension of the pyridinium salt (1 g.), lithium aluminium hydride (0·6 g.), and aluminium trichloride (1 g.) in dry ether (100 ml.) was stirred at room temperature for 24 hr. Basic material was isolated and worked up by preparative g.l.c. The major component (85%) was N-2-(3-*benzo*[b]*thienyl*)*ethyl*-1,2,3,6-*tetrahydropyridine* (12) (Found: *M*, 243·1083. $C_{15}H_{17}NS$ requires *M*, 243·1082), $\lambda_{max.}$ 230 (ε 30,000), 251infl (3200), 261 (4900), 269infl (4400), 291 (3000), and 299 (3600) nm.; see text for n.m.r. data. The *hydrochloride* crystallised from ethanol–ether as white needles, m.p. 230—232° (Found: C, 64·3; H, 6·3; N, 5·0. $C_{15}H_{18}ClNS$ requires C, 64·4; H, 6·5; N, 5·0%), $\nu_{max.}$ 2580 cm.$^{-1}$ ($NH^+$).

The minor component (15%) was not purified satisfactorily, but the mass spectrum and g.l.c. retention time were similar to those of the piperidine derivative (13).

*Identification of the Tetrahydropyridine* (12).—The product just described was hydrogenated in ethanol in the presence of 5% palladised charcoal (uptake 1·05 mol.). The resulting oil was converted into the hydrochloride, m.p. 280—282°, undepressed on admixture with authentic *N*-2-(3-benzo[*b*]thienyl)ethylpiperidine hydrochloride.

3-*Acetyl*-N-2-(3-*benzo*[b]*thienyl*)*ethylpyridinium Bromide* (10).—3-(2-Bromoethyl)benzo[*b*]thiophen (10 g.) and 3-acetylpyridine (18 ml.) were heated together under nitrogen for 15 hr. at 80°. The resulting crystalline mass was triturated with ether and recrystallised from ethanol, to give the *salt* as tan cubes (10·5 g., 70%), m.p. 206—207° (Found: C, 56·4; H, 4·3; N, 3·7. $C_{17}H_{16}BrNOS$ requires C, 56·35; H, 4·45; N, 3·85%), $\nu_{max.}$ 1700 cm.$^{-1}$ (C=O).

*Preparation and Cyclisation of* 5-*Acetyl*-N-2-(3-*benzo*[b]-*thienyl*)*ethyl*-1,2,3,4-*tetrahydropyridine* (15).—A solution of the pyridinium salt just described (2 g.) in 50% aqueous ethanol (200 ml.) was shaken with hydrogen for 6 hr. (uptake 1·95 mol.) in the presence of 5% palladised charcoal. The catalyst was filtered off, the solvent was removed under reduced pressure, and the oily product was isolated as the *hydrochloride* (1·3 g., 73%), m.p. 165—167° (white needles from ethanol–ether) (Found: C, 63·5; H, 6·0; N, 4·5. $C_{17}H_{20}ClNOS$ requires C, 63·45; H, 6·25; N, 4·35%), $\nu_{max.}$ 2540 ($NH^+$) and 1600 (C=O) cm.$^{-1}$, $\lambda_{max.}$ (free base) 227 (ε 28,050) and 291 (16,800) nm., δ (free base) 6·89 and 7·10 (each 1H, s, C:CH), and 1·92 (3H, s, Ac) p.p.m.

A solution of the hydrochloride (0·7 g.) in concentrated hydrochloric acid (50 ml.) was heated under reflux for 3 hr., cooled, and basified with aqueous sodium hydroxide. The tetracyclic compound (7) was extracted with ether and isolated as the *hydrochloride* (0·5 g., 71%), which formed white needles, m.p. 218—220° (from ethanol–ether) (Found: C, 63·5; H, 6·3; N, 4·4%), $\nu_{max.}$ 2540 ($NH^+$) and 1710 (C=O) cm.$^{-1}$, $\lambda_{max.}$ (free base) 233 (ε 28,400), 239infl (22,800), 267 (7250), 291 (3200), and 299 (2950) nm., δ (free base) 2·02 p.p.m. (3H, s, Ac) (no vinylic resonance).

*Cyclisation of* N-2-(3-*Benzo*[b]*thienyl*)*ethylpiperidine* (13).—A solution of the piperidine derivative (13) (1·0 g., 0·0041 mole) and mercury(II) acetate (14·0 g., 0·044 mole) in 5% aqueous acetic acid (50 ml.) was kept at 100° for 1 hr., then treated for 1 hr. with hydrogen sulphide, and filtered. The filtrate was evaporated to small volume, diluted with 50% aqueous ethanol (100 ml.), and brought to pH 6 with sodium hydrogen carbonate. The mixture was kept overnight with an excess of sodium borohydride, concentrated to 50 ml., basified with aqueous sodium hydroxide, and shaken with chloroform. Removal of the solvent gave the *base* (6), which crystallised from light petroleum (charcoal) as pale yellow cubes (0·65 g., 65%), m.p. 80—81°. An analytical sample, purified by short-path distillation at 130—140° (bath)/4 mm., had m.p. 83—84° (Found: C, 73·9; H, 7·0; N, 5·6; S, 13·3%; *M*, 243. $C_{15}H_{17}NS$ requires C, 74·0; H, 7·05; N, 5·75; S, 13·2%; *M*, 243); no vinyl resonance in the n.m.r. spectrum.

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