Synthesis of 4*H*-Cyclohepta[*b*]thiophen-4-ones, 4*H*-Cyclohepta[*b*]furan-4-one, and 9*H*-Cyclohepta[*b*]pyridin-9-one

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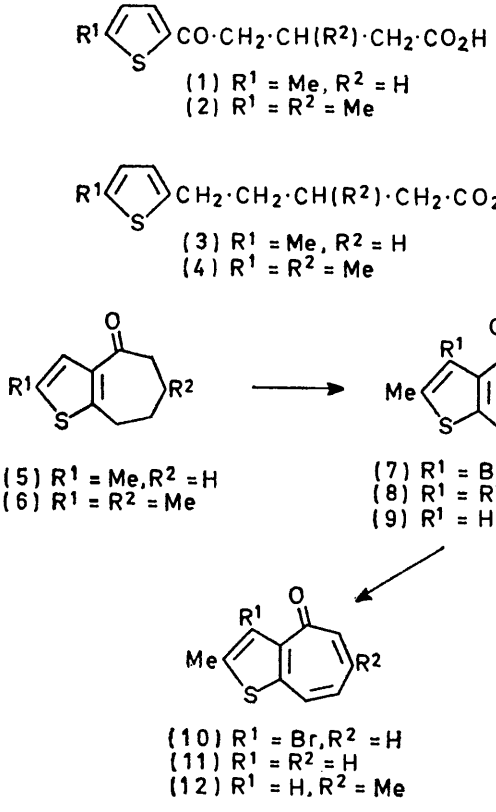
The title compounds have been prepared by dehydrobromination of αα-dibromocycloheptanones, using lithium salts in boiling dimethylformamide. Conversion of 6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyridine into 5,6,7,8-tetrahydro-9*H*-cyclohepta[*b*]pyridin-9-one (20) was achieved *via* the *N*-oxide (21) and the 9-hydroxy-derivative (23).

ONE of us (G. J.) has reported [1] a convenient preparation of tropones from cycloheptanones, *via* the 2,2,6-tribromo-derivatives, using lithium salts in dimethylformamide (DMF) as dehydrobrominating agents. Similar dehydrobromination of αα-dibromo-ketones gave high yields of benztropones [2,3] and pyrroloazepinones or azepinoindolones.[4] As part of an investigation of the properties of tropones with fused heterocyclic rings we



have prepared some 4*H*-cyclohepta[*b*]thiophen-4-ones, 4*H*-cyclohepta[*b*]furan-4-one, and 9*H*-cyclohepta[*b*]pyridin-9-one, by the lithium salt dehydrobromination of suitable αα-dibromo-ketones, providing further evidence of the scope of this procedure.

The tetrahydro-4*H*-cyclohepta[*b*]thiophen-4-ones (5) [5] and (6) were prepared by well established routes. Acylation of 2-methylthiophen with glutaric anhydride or β-methylglutaric anhydride gave the keto-acids (1) and (2), reduced by the Huang-Minlon procedure to the pentanoic acids (3) and (4). The acid chlorides were cyclised, using stannic chloride, to give the cyclic ketones (5) and (6). Bromine in carbon tetrachloride converted the ketone (5) into the tribromo-derivative (7); with phenyltrimethylammonium tribromide (PTAB) both ketones (5) and (6) gave a dibromo-derivative, respectively (8) and (9). The position of bromination in the three bromo-derivatives was established by the n.m.r. spectra; all three showed the loss of the signal due to the C(5) methylene group, and the tribromo-ketone (7) showed no signal in the aromatic region. When treated with lithium chloride or carbonate in boiling DMF all three bromo-ketones were dehydrobrominated in high yield. The products were the thienotropones (10)—(12). All three showed i.r. absorption near 1630 and 1590 cm^{-1}; the u.v. absorption spectra were similar, with the expected bathochromic shift on protonation (Table 1).

TABLE 1

U.v. and visible spectra of tropones

Compound	Solvent *	$\lambda_{max.}$/nm (log ε)
Benztropone †	E	229 (4·33), 260sh, 307sh, 320 (3·81), 343sh
	S (60%)	230sh, 252sh, 266 (4·55), 285 (4·09), 293 (4·07), 330 (3·52), 401 (3·72)
(10)	E	245 (4·29), 268sh, 335 (3·95)
(10)	S	225 (4·10), 253 (4·43), 283 (4·34), 356 (4·76), 421 (4·63)
(11)	E	242 (4·27), 330 (3·93), 350 (3·90), 365 (3·88)
(11)	S	247 (4·02), 275 (4·03), 293sh, 325 (3·33), 335 (3·38), 405 (3·47)
(12)	E	245 (4·87), 332 (4·38), 344sh, 360 (4·31)
(15)	E	244sh, 259sh, 270sh, 300 (3·72), 311 (3·79), 341 (3·83), 355 (3·80), 372sh
(27)	E	220 (4·57), 256sh, 321sh, 338 (4·20)

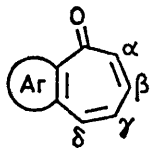
* E = ethanol, S = sulphuric acid. † J. Büchi, H. Dietrich, and E. Eichenberger, *Helv. Chim. Acta*, 1956, **39**, 957.

By condensation of 2-furylacrylaldehyde with ethyl acetate,[6] reduction of the resulting 2-furylpentadienoate,[7] and hydrolysis of the saturated ester, 5-(2-furyl)-

[1] G. Jones, *J. Chem. Soc.* (*C*), 1970, 1230.
[2] E. W. Collington and G. Jones, *Chem. Comm.*, 1968, 958.
[3] E. W. Collington and G. Jones, *J. Chem. Soc.* (*C*), 1969, 2656.
[4] E. W. Collington and G. Jones, *J. Chem. Soc.* (*C*), 1969, 1028.
[5] P. Cagniant and D. Cagniant, *Bull. Soc. chim. France*, 1956, 1152.
[6] A. Hinz, G. Meyer, and G. Schücking, *Ber.*, 1943, **76**, 676.
[7] W. Treibs and W. Heyer, *Chem. Ber.*, 1954, **87**, 1197.

TABLE 2

N.m.r. data of tropones



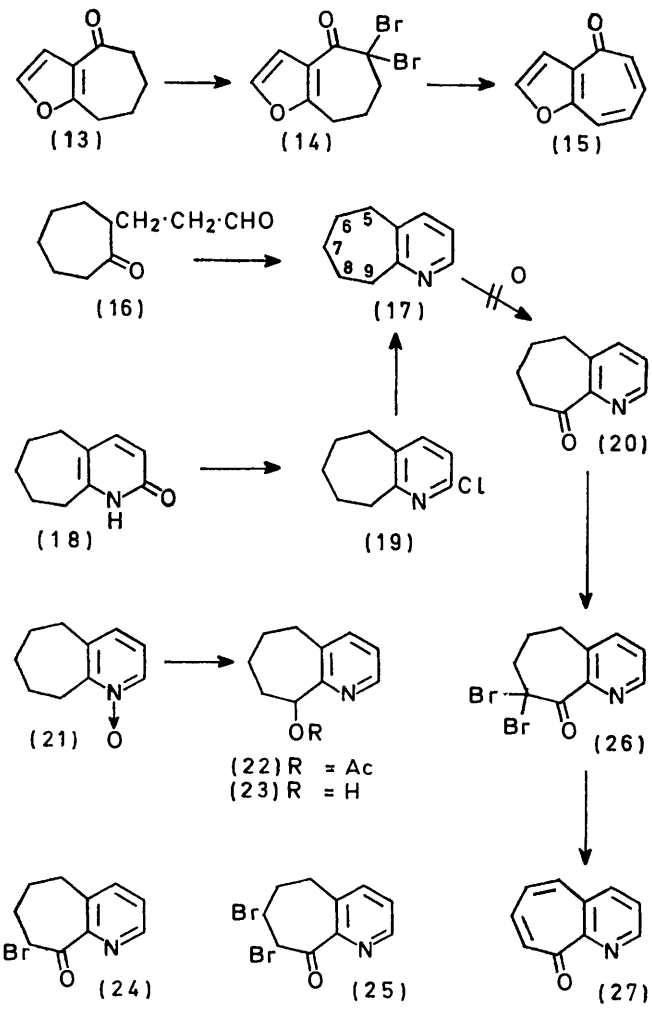
Compound	Chemical shifts δ (p.p.m.) ($CDCl_3$) Aromatic	α	β	γ	δ	Others	J/Hz
Benztropone †		← 7·0 →		6·8m	7·3q		$J_{\alpha\beta}$ 11·5, $J_{\beta\gamma}$ 8·3, $J_{\gamma\delta}$ 11·3, $J_{\alpha\gamma}$ 1·2, $J_{\beta\delta}$ 1·2
(10)	None	← 6·8—7·0 →		6·55q	7·14d	2·5 (3H,s)	$J_{\beta\gamma}$ 6, $J_{\gamma\delta}$ 10
(11)	7·5 (1H,s)	← 6·8—7·1 →		6·7m	7·26d	2·55 (3H,s)	$J_{\gamma\delta}$ 11
(12)	7·5 (1H,s)	6·9s		6·5d	7·2d	2·3 (3H,s) 2·5 (3H,s)	$J_{\gamma\delta}$ 11
(15)	7·7(1H,d) 7·22(1H,d)	7·15q	7·25m	6·85m	7·48q		$J_{\alpha\beta}$ 12, $J_{\beta\gamma}$ 8, $J_{\gamma\delta}$ 11, $J_{\alpha\gamma}$ 1·5, $J_{\beta\delta}$ 1; $J_{2,3}$ 2
(27)	9·1q, 8·1q, 7·7m	← 7·0—7·2 →		6·8m	7·3q		

† D. J. Bertelli, J. T. Gerig, and J. M. Herbelin, *J. Amer. Chem. Soc.*, 1968, **90**, 107.

pentanoic acid is readily available. Cyclisation of the acid chloride gave 5,6,7,8-tetrahydro-4*H*-cyclohepta-[*b*]furan-4-one (13), which was brominated slowly by PTAB to give the 5,5-dibromo-derivative (14). Dehydrobromination with lithium carbonate in boiling DMF gave 4*H*-cyclohepta[*b*]furan-4-one (15); spectral data for this tropone are given in Tables 1 and 2.

A route from 6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]-pyridine (17) was used to obtain the cyclohepta[*b*]-pyridin-9-one (20). To obtain the cyclohepta[*b*]pyridine (17) two methods were used. The keto-aldehyde (16) can be obtained from acrylaldehyde and a cycloheptanone enamine;[8] the keto-aldehyde reacted with hydroxylamine to give a good yield of cycloheptapyridine (17). A longer route started from 2-formylcycloheptanone;[9] the penultimate stage, the conversion of the pyridone (18) into the chloropyridine (19) was considerably improved by using dichloro(phenyl)-phosphine oxide in place of phosphoryl chloride.

A common route to 2-pyridyl ketones is by selenium dioxide oxidation of the corresponding 2-pyridylalkane, but under a variety of conditions with selenium dioxide the tetrahydrocyclohepta[*b*]pyridine (17) gave no evidence of oxidation to the ketone (20). The *N*-oxide (21), when treated with acetic anhydride, gave the 9-acetoxycyclohepta[*b*]pyridine (22), which was hydrolysed to the alcohol (23). Again oxidation proved difficult, no reaction being observed when the alcohol (23) was treated with neutral permanganate, with aluminium isopropoxide, or with activated manganese dioxide. Reaction between the alcohol (23) and *N*-bromosuccinimide gave three products, the ketone (20), and two brominated ketones (24) and (25). The assignment of structures (24) and (25) rests on spectroscopic evidence. Both compounds showed carbonyl absorption above 1705 cm^{-1}, compared with 1690 cm^{-1} for the ketone (20). The monobromo-ketone (24) had a characteristic triplet at δ 5·45 p.p.m. (1H) indicative



[8] R. D. Allen, B. G. Cordiner, and R. J. Weels, *Tetrahedron Letters*, 1968, 6055.
[9] E. Godar and R. P. Mariella, *J. Amer. Chem. Soc.*, 1957, **79**, 1402.

of the system CO·CHBr·CH_2; the dibromo-ketone (25) had a doublet at δ 4·87 and a multiplet at δ 5·75 p.p.m., a pattern of shift and coupling previously observed for the system CO·CHBr·CHBr in the benzocycloheptanone series.[3] The cycloheptapyridinone (20) was brominated in low yield (using PTAB) to give 8,8-dibromo-5,6,7,8-tetrahydro-9*H*-cyclohepta[*b*]pyridin-9-one (26); no attempt has been made to obtain the optimum yield. Dehydrobromination using lithium carbonate in boiling DMF gave 9*H*-cyclohepta[*b*]pyridin-9-one (27).

The n.m.r. spectra of the various tropones are grouped in Table 2. The similarities between the chemical shifts and the coupling constants for the hydrogen atoms on the seven-membered rings are noteworthy, bearing in mind the very different electron availability in the fused aromatic rings. Since the aromatic protons also show no abnormality, we assume that there is little delocalisation over the whole fused system, in keeping with the reported lack of aromatic character in the tropone ring system.

EXPERIMENTAL

All m.p.s were determined on a Kofler heated stage. Chromatography was carried out on columns of alumina (Woelm, activity in parentheses), or on 40 × 20 cm plates of Merck Kieselgel PF_{254}. N.m.r. shifts are p.p.m. from tetramethylsilane.

5-(5-*Methyl*-2-*thienyl*)-5-*oxopentanoic Acid* (1).—Prepared as described,[10] the acid (1) had m.p. 119° (lit.,[10] 118°), δ ($CDCl_3$) 1·9—2·3 (4H, m), 2·4 (3H, s), 2·9 (2H, t), 6·8 (1H, d, *J* 4 Hz), 7·6 (1H, d, *J* 4 Hz), and 10·8 p.p.m. (1H, s, CO_2H).

3-*Methyl*-5-(5-*methyl*-2-*thienyl*)-5-*oxopentanoic Acid* (2).—To a vigorously stirred solution of 2-methylthiophen (27·5 g) and β-methylglutaric anhydride (30 g) in nitrobenzene (250 ml) at 0° was added aluminium chloride (74 g) (over 1 h). The mixture was stirred (1 h), then hydrolysed with ice–hydrochloric acid. Steam distillation removed the nitrobenzene, and the crude product was isolated by filtration. Recrystallisation from benzene–petroleum (b.p. 60—80°) gave the *keto-acid* (2), m.p. 79—80° (36 g, 70%) (Found: C, 57·9; H, 6·15. $C_{11}H_{14}O_3S$ requires C, 58·4; H, 6·25%), $\nu_{max.}$ ($CHCl_3$) 1710 and 1650 cm^{-1}, $\lambda_{max.}$ (EtOH) 264 and 296 nm (log ε 3·90 and 3·99), δ ($CDCl_3$) 1·1 (3H, d, *J* 5 Hz, $CHCH_3$), 2·4 (3H, m), 2·5 (3H, s), 2·8 (2H, m, $CO{\cdot}CH_2$), 6·8 (1H, d, *J* 5 Hz), 7·6 (1H, d, *J* 5 Hz), and 10·8 p.p.m. (1H, s, CO_2H).

On a scale 10% of that reported above, the yield of acid (2) was 93%.

5-(5-*Methyl*-2-*thienyl*)*pentanoic Acid* (3).—The method described for a similar Huang-Minlon reduction[11] was used; acid (1) gave a 60% yield of pentanoic acid (3), b.p. 160—162° at 0·5 mmHg, m.p. 57° (lit.,[5] b.p. 200° at 17 mmHg, m.p. 57·5°), δ (CCl_4) 1·6—2·0 (4H, m), 2·5 (3H, s), 2·45 (2H, m), 2·85 (2H, m), 6·7br (2H, s), and 11·5 p.p.m. (1H, s, CO_2H).

3-*Methyl*-5-(5-*methyl*-2-*thienyl*)*pentanoic Acid* (4).—A solution of the keto-acid (2) (16·3 g) and 100% hydrazine hydrate (9·2 ml) in diethylene glycol (100 ml) and water (5 ml) was heated with distillation to 180°. The mixture was cooled to 100°, potassium hydroxide (14 g) was added, and the mixture was boiled under reflux (4 h). The cooled mixture was poured into water and washed with ether; the aqueous layer was acidified, and the product was extracted with ether. The dried (Na_2SO_4) solution was distilled to give the *methylpentanoic acid* (4), b.p. 150—152° at 1 mmHg, m.p. 43—44° [from petroleum (b.p. 40—60°)] (6·4 g, 42%) (Found: C, 62·0; H, 7·65. $C_{11}H_{16}O_2S$ requires C, 62·2; H, 7·60%), $\nu_{max.}$ ($CHCl_3$) 1710 cm^{-1}, $\lambda_{max.}$ (EtOH) 233 nm (log ε 2·87), δ ($CDCl_3$) 1·1 (3H, d, *J* 5 Hz, $CHCH_3$), 1·6—1·9 (2H, m), 2·0—2·3 (3H, m), 2·4 (3H, s), 2·8 (2H, t), 6·6br (2H, s), and 10·7 p.p.m. (1H, s, CO_2H).

5,6,7,8-*Tetrahydro*-2-*methyl*-4H-*cyclohepta*[b]*thiophen*-4-*one* (5).—Prepared as described,[12] the ketone (5) had b.p. 108° at 1·3 mmHg (lit.,[5] 157° at 7 mmHg), δ (CCl_4) 1·7—1·9 (4H, m), 2·3 (3H, s), 2·4—2·6 (2H, m, H5), 2·8—3·0 (2H, m, H8), and 6·9 p.p.m. (1H, s).

5,6,7,8-*Tetrahydro*-2,6-*dimethyl*-4H-*cyclohepta*[b]*thiophen*-4-*one* (6).—To a solution of the pentanoic acid (4) (24 g) in ether (100 ml), purified thionyl chloride (18 ml) and pyridine (several drops) were added. The mixture was boiled (5 h) after which solvent and the excess of thionyl chloride were removed *in vacuo*. The crude acid chloride was dissolved in dry carbon disulphide (500 ml) and to the cooled (0°) solution stannic chloride (25 ml) was added dropwise with vigorous stirring. The mixture was then allowed to come to room temperature and stirred (2·5 h). Ice and hydrochloric acid were added, and the organic layer was separated, dried, and distilled under nitrogen, to give the *cycloheptathiophenone* (6), b.p. 121—124° at 1·5 mmHg (13·7 g, 63%), which slowly solidified (Found: C, 68·1; H, 7·3. $C_{11}H_{14}OS$ requires C, 68·0; H, 7·25%), $\nu_{max.}$ (CCl_4) 1670 cm^{-1}, $\lambda_{max.}$ (EtOH) 226, 256, and 283sh nm (log ε 4·12, 4·08, —), δ (CCl_4) 1·1 (3H, d) 1·8—2·3 (3H, m), 2·4 (3H, s), 2·5—2·7 (2H, m, $CH_2{\cdot}CO$), 3·0 (2H, t, *J* 6 Hz, H8), and 7·2 p.p.m. (1H, s).

3,5,5-*Tribromo*-5,6,7,8-*tetrahydro*-2,6-*dimethyl*-4H-*cyclohepta*[b]*thiophen*-4-*one* (7).—A solution of bromine (6·5 ml) in carbon tetrachloride (30 ml) was added dropwise to a stirred solution of the cyclic ketone (5) (7·5 g) in carbon tetrachloride (50 ml) containing potassium carbonate (17·4 g). The mixture was stirred overnight and filtered; the solid was washed with chloroform and the total organic solutions were evaporated. Recrystallised from methanol, the *tribromo-ketone* (7) had m.p. 132° (16·5 g, 95%) (Found: C, 29·1; H, 3·0. $C_{10}H_9Br_3OS$ requires C, 28·8; H, 2·2%), $\nu_{max.}$ (Nujol) 1720 cm^{-1}, $\lambda_{max.}$ 232sh and 268 nm (log ε —, 3·32), δ ($CDCl_3$) 2·0—2·2 (2H, m), 2·4 (3H, s), and 2·9—3·1 p.p.m. (4H, m).

5,5-*Dibromo*-5,6,7,8-*tetrahydro*-2-*methyl*-4H-*cyclohepta*[b]-*thiophen*-4-*one* (8).—To a solution of the cyclic ketone (5) (1 g) in dry tetrahydrofuran (THF) (30 ml) at room temperature, was added phenyltrimethylammonium tribromide (PTAB) (4·2 g). After 24 h at room temperature the mixture was filtered, the solid was washed with THF, and the combined THF solutions were evaporated. The solid *dibromo-ketone* (8), crystallised from methanol, had m.p. 79—80° (1·6 g, 85%) (Found: C, 35·9; H, 2·9. $C_{10}H_{10}$-

[10] J. F. McGhie, W. A. Ross, D. Evans, and J. E. Tomlin, *J. Chem. Soc.*, 1962, 350.

[11] G. M. Badger, H. J. Rodda, and W. H. F. Sasse, *J. Chem. Soc.*, 1954, 4162.

[12] P. Cagniant and D. Cagniant, *Bull. Soc. chim. France*, 1955, 680.

Br_2OS requires C, 35·5; H, 3·0%), $\nu_{max.}$ (Nujol) 1670 cm^{-1}; $\lambda_{max.}$ 230sh and 266 nm (log ε —, 3·38), δ ($CDCl_3$) 2·0—2·2 (2H, m), 2·3 (3H, s), 3·0—3·4 (4H, m), and 7·0 p.p.m. (1H, s).

5,5-Dibromo-5,6,7,8-tetrahydro-2,6-dimethyl-4H-cyclohepta[b]*thiophen-4-one* (9).—Prepared as described for compound (8) starting from cyclic ketone (6) (4 h reaction time), in 70% yield, the *dibromo-ketone* (9) had m.p. 69—70° (from methanol) (Found: C, 37·7; H, 3·9. $C_{11}H_{12}Br_2OS$ requires C, 37·5; H, 3·45%), $\nu_{max.}$ ($CHCl_3$) 1670 cm^{-1}, $\lambda_{max.}$ (EtOH) 229sh, 265, and 305sh (log ε —, 2·84, —), δ ($CDCl_3$) 1·4 (3H, d, *J* 6 Hz, $CHCH_3$), 1·6—2·2 (2H, m), 2·5 (3H, s), 2·6—3·2 (3H, m), and 6·97 p.p.m. (1H, s).

3-Bromo-2-methyl-4H-cyclohepta[b]*thiophen-4-one* (10).—A mixture of the tribromo-ketone (7) (5 g) and lithium chloride (1·5 g) in DMF (50 ml) was vigorously boiled under nitrogen for 2 h. Removal of the solvent under reduced pressure, followed by dilution of the residue with water gave a product, extracted by chloroform. The dried solution was evaporated, and the residue crystallised from methanol to give the *bromotropone* (10), m.p. 144—145° (1·85 g, 60%) (Found: C, 47·0; H, 2·9. $C_{10}H_7BrOS$ requires C, 47·1; H, 2·8%), $\nu_{max.}$ ($CHCl_3$) 1630 and 1590 cm^{-1}. U.v. and n.m.r. data are given in Tables 1 and 2.

2-Methyl-4H-cyclohepta[b]*thiophen-4-one* (11).—A solution of the dibromo-ketone (8) (5 g) and lithium carbonate (3·5 g) in anhydrous DMF was boiled (2·5 h) and worked up as described for compound (10). The *methyltropone* (11), m.p. 64—65° (from cyclohexane), was obtained in 77% yield (Found: C, 68·0; H, 4·65. $C_{10}H_8OS$ requires C, 68·2; H, 4·55%), $\nu_{max.}$ (CCl_4) 1630 and 1590 cm^{-1}. U.v. and n.m.r. data are given in Tables 1 and 2.

2,6-Dimethyl-4H-cyclohepta[b]*thiophen-4-one* (12).—From the dibromo-ketone (9) (1 g) and lithium carbonate (0·5 g), the *dimethyltropone* (12), m.p. 132—133° [from petroleum (b.p. 60—80°)], was obtained in 83% yield (*m/e* 190·0446. $C_{11}H_{10}OS$ requires *M* 190·0453), $\nu_{max.}$ ($CHCl_3$) 1620 and 1560 cm^{-1}. U.v. and n.m.r. data are given in Tables 1 and 2.

5,6,7,8-Tetrahydro-4H-cyclohepta[b]*furan-4-one* (13).—The ketone (13) was synthesised from furfural *via* 2-furylacrylaldehyde,[13] ethyl 5-(2-furyl)pentadienoate,[6] 5-(2-furyl)-pentanoic acid,[7] and the acid chloride.[7]

5,5-Dibromo-5,6,7,8-tetrahydro-4H-cyclohepta[b]*furan-4-one* (14).—Bromination of the cycloheptafuranone (13) by PTAB in tetrahydrofuran proceeded slowly (at least 5 h) and it was found necessary to add a considerable excess of PTAB. Decomposition of the excess of reagent with acetone, followed by filtration and evaporation of the filtrate gave a gum, which solidified when triturated with methanol to give the *dibromocycloheptafuranone* (14) (60%), m.p. 113—114° (from methanol) (Found: C, 35·0; H, 2·45. $C_9H_8Br_2O_2$ requires C, 35·1; H, 2·6%), $\nu_{max.}$ (CCl_4) 1670 cm^{-1}, $\lambda_{max.}$ (EtOH) 228sh and 290 nm (log ε —, 3·72), δ ($CDCl_3$) 2·0—2·4 (2H, m), 3·1 (4H, t, H-6 and H-8), 6·8 (1H, d, *J* 2 Hz, H-3), and 7·3 p.p.m. (1H, d, *J* 2 Hz, H-2).

4H-Cyclohepta[b]*furan-4-one* (15).—From the dibromo-ketone (14) (3 g) and lithium carbonate (1·5 g) in anhydrous DMF (50 ml) (3 h) a total of 0·78 g of crude (once-distilled, b.p. 110° at 0·5 mmHg) furotropone (52%) was obtained. For analysis, a sample was purified by p.l.c. ($CHCl_3$–benzene, 1 : 1, two runs); the major band was extracted with methanol, and the residue, after evaporation, was distilled (bulb-tube) to give the *furotropone* (15), m.p. 39—41° (Found: C, 73·7; H, 4·1. $C_9H_6O_2$ requires C, 73·95; H, 4·15%), $\nu_{max.}$ (CCl_4) 1630 and 1595 cm^{-1}. U.v. and n.m.r. data are given in Tables 1 and 2.

6,7,8,9-Tetrahydro-5H-cyclohepta[b]*pyridine* (17).—(*a*) A solution of the keto-aldehyde [8] (16) (10 g) and hydroxylamine hydrochloride (5 g) in ethanol (10 ml) was boiled (3 h), then evaporated, and the residue was neutralised and extracted with ether. The dried extract was distilled, the cyclohepta[*b*]pyridine (17) having b.p. 107—109° at 15 mmHg (lit.,[14] b.p. 111·5—112° at 16 mmHg) (9·9 g, 88%).

(*b*) A solution of the pyridone (18) (10 g) in dichloro(phenyl)phosphine oxide (14·7 g) was heated at 180° (2 h), cooled, and poured into ice–water (150 ml). The aqueous mixture was neutralised (sodium hydroxide), and steam-distilled, giving the chloropyridine (19), m.p. 194—195° (lit.,[9] 194—194·5°) (8·9 g, 81%). Reduction as described [9] gave the cycloheptapyridine (17).

6,7,8,9-Tetrahydro-5H-cyclohepta[b]*pyridine N-Oxide* (21).—A solution of the cyclohepta[*b*]pyridine (17) (10 g) in glacial acetic acid (70 ml) with hydrogen peroxide (30%; 9 ml) was heated at 100° (9 h). More hydrogen peroxide (5 ml) was added, and heating continued (6 h). Evaporation under reduced pressure gave an oil, which was neutralised (sodium hydrogen carbonate) and extracted with chloroform. Distillation of the residue after removal of the chloroform gave the N-*oxide* (21), b.p. 124° at 0·03 mmHg, m.p. 107—108° (10·5 g, 95%) (Found: C, 73·6; H, 8·4; N, 8·3. $C_{10}H_{13}NO$ requires C, 73·6; H, 8·0; N, 8·6%), $\lambda_{max.}$ (EtOH) 221 and 264 nm (log ε 4·36 and 4·02), *m/e* 163 (M^+), 146, 130, and 128, δ ($CDCl_3$) 1·8 (6H, m), 2·8 (2H, m), 3·4 (2H, m), 7·05br (2H, s), and 8·15 p.p.m. (1H, t).

6,7,8,9-Tetrahydro-5H-cyclohepta[b]*pyridin-9-ol* (23).—(*a*) A solution of the *N*-oxide (21) (10 g) in acetic anhydride (40 ml) was heated on a water-bath (2·5 h), the acetic anhydride was evaporated off under reduced pressure, and the residue was distilled to give the acetoxycycloheptapyridine (22), b.p. 106° at 0·6 mmHg (8·8 g, 78%), $\nu_{max.}$ ($CHCl_3$) 1735 cm^{-1}, $\lambda_{max.}$ (EtOH) 207, 249, and 290 nm (log ε 3·85, 3·64, and 3·46), δ ($CDCl_3$) 1·9 (9H, m), 2·85 (2H, m), 6·0 (1H, m, CH·OAc), 7·1 (1H, dd), 7·45 (1H, dd), and 8·4 p.p.m. (1H, dd). A fore-run contained the deoxygenated material, cyclohepta[*b*]pyridine (17) (1·4 g, 19%).

(*b*) The acetoxy-compound (22) (5 g) was heated on a water-bath with aqueous potassium hydroxide (25 ml; 3 h). The cooled solution was extracted with chloroform, the chloroform solution was dried and evaporated, and the residue was distilled to give the *cycloheptapyridin-9-ol* (23), b.p. 91—93° at 0·4 mmHg (3·0 g, 76%) (Found: C, 73·6; H, 8·1; N, 8·6. $C_{10}H_{13}NO$ requires C, 73·6; H, 8·0; N, 8·6%), $\nu_{max.}$ ($CHCl_3$) 3360 cm^{-1}, $\lambda_{max.}$ (EtOH) 210, 263, and 290sh nm (log ε 3·75, 3·62, —), δ ($CDCl_3$) 1·25 (2H, m), 1·85 (4H, m), 2·7 (2H, m), 4·75 (1H, d), 5·8br (1H, s, OH), 7·0 (1H, dd), 7·4 (1H, dd), and 8·3 p.p.m. (1H, dd).

Reaction between Alcohol (23) *and N-Bromosuccinimide.*—A solution of the alcohol (23) (2 g) in carbon tetrachloride (40 ml) with *N*-bromosuccinimide (2 g) was boiled over a 200 W lamp until t.l.c. showed all the alcohol to have reacted. The cooled solution was filtered, washed with aqueous sodium hydrogen carbonate, then water, dried, and evaporated. The residue was chromatographed on

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alumina (3); elution with benzene and with chloroform gave mixtures, which were combined, and separated by p.l.c. (chloroform). Three major bands (A—C) were obtained with increasing R_F values. *Band A* was extracted with methanol; evaporation of methanol gave as an oil the *cycloheptapyridin-9-one* (20), b.p. 125° at 0·3 mmHg (bulb-tube) (0·5 g, 25%) (Found: C, 74·2; H, 6·4; N, 8·3. $C_{10}H_{11}NO$ requires C, 74·5; H, 6·8; N, 8·7%), $\nu_{max.}$ (film) 1695 cm^{-1}, $\lambda_{max.}$ (EtOH) 209, 228, and 274 nm (log ε 3·64, 3·64, and 3·51), δ ($CDCl_3$) 1·9 (4H, m), 2·85 (4H, m), 7·35 (1H, dd), 7·65 (1H, dd), and 8·65 p.p.m. (1H, dd), *m/e* 161 (M^+), 133, 105, and 92. *Band B*, after extraction and evaporation gave the 8-bromocycloheptapyridine-9-one (24) (0·1 g, 10%), $\nu_{max.}$ (film) 1710 cm^{-1}, δ ($CDCl_3$) 2·25 (4H, m), 2·9 (2H, m), 5·45 (1H, m, COCHBr), 7·4 (1H, dd), 7·9 (1H, d), and 8·7 p.p.m. (1H, dd), *m/e* 241, 239 (M^+), 133, 131, 119, 117, and 107. *Band C*, after extraction and evaporation gave the dibromo-ketone (25) as an oil (500 mg, 30%), $\nu_{max.}$ (film) 1720 cm^{-1}, δ ($CDCl_3$) 1·95 (2H, m), 2·95 (2H, m), 4·87 (1H, m, CHBr), 5·75 (1H, d, CO·C*H*Br·CHBr), 7·15 (1H, dd), 7·5 (1H, d), and 8·4 p.p.m. (1H, dd), *m/e* 321, 319, and 317 (M^+).

8,8-*Dibromo*-6,7,8,9-*tetrahydro*-9H-*cyclohepta*[b]*pyridin*-9-*one* (26).—A solution of the ketone (20) (0·3 g) and PTAB (1·4 g) in dry THF (30 ml) was stirred for 26 h; the solvent was removed, and the residue treated with saturated aqueous sodium hydrogen carbonate and extracted with chloroform. The dried extracts were evaporated to give a pale red oil, which was chromatographed on alumina (3); elution with benzene gave the *dibromo-ketone* (26) (0·08 g, 14%), m.p. 83—84° (from methanol) (Found: C, 38·0; H, 3·3; N, 4·1. $C_{10}H_9Br_2NO$ requires C, 37·6; H, 2·9; N, 4·4%), $\nu_{max.}$ ($CHCl_3$) 1718 cm^{-1}, $\lambda_{max.}$ (EtOH) 211, 264, and 270sh (log ε 3·85, 3·58, —), δ ($CDCl_3$) 2·1 (2H, m), 2·8 (4H, m), 7·5 (2H, m), and 8·6 p.p.m. (1H, m), *m/e* 321, 319, 317 (M^+), 240, and 238.

9H-*Cyclohepta*[b]*pyridin*-9-*one* (27).—Prepared from the dibromo-compound (0·28 g) and lithium carbonate (0·15 g) in dry DMF (2 h boiling), the *cycloheptapyridin-9-one* (27) was isolated by chromatography on alumina (3), eluted with chloroform–benzene (9 : 1) (0·65 g, 46%) (Found: C, 76·0; H, 4·8; N, 8·7. $C_{10}H_7NO$ requires C, 76·4; H, 4·5; N, 8·9%), $\nu_{max.}$ ($CHCl_3$) 1642, 1612, and 1588 cm^{-1}; u.v. and n.m.r. data in Tables 1 and 2, *m/e* 157 (M^+), 129, 102, and 83.

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