The Synthesis and Photochemical Behaviour of Some Annelated Tropones

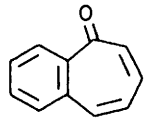
Martin G. Hicks, Gurnos Jones *, and Hamid Sheikh
Department of Chemistry, University of Keele, Keele, Staffordshire ST5 5BG

The synthesis of 2-methoxy- (**12**), 2-methoxy-6-bromo- (**13**), 1-methoxy-4-methyl- (**22**), 3-amino- (**33**), 3-amino-2,4-dibromo- (**35**), and 3-methoxy-benzotropone (**36**) is reported; on irradiation of these and other benzotropones, the presence of an electron-donating group at position 1 or 3 was found to aid electrocyclization. Four new dihydrocyclobut[*a*]inden-7-ones (**61**)—(**64**) were thus obtained. The pyrido[*b*]tropones (**44**), (**48**), and (**49**) and the pyrido[*c*]tropones (**59**) and (**60**) were also synthesized; none gave electrocyclic reactions when irradiated.

Since our discovery of a high yielding conversion of benzocycloheptanones into benzotropones,[1,2] a number of annelated tropones have been prepared using our procedure.[3,4] We have investigated the behaviour of benzotropone (**1**)[2] and the thienotropones (**3**)[5] under u.v. irradiation; the former undergoes an electrocyclic reaction to give the tricyclic compound (**2**), as do a number of benzotropones with substituents on the seven-membered ring.[6] The latter mainly form $4\pi_s + 2\pi_s$ dimers, with the exception of compound (**3**; $R^1 = R^2 = Me$), which gave the tricyclic compound (**4**).[5] We assumed the 'normal' photochemical reaction of thienotropones to be dimerisation; to discover some of the factors controlling the mode of photochemical reaction in annelated tropones we have synthesized a number of benzotropones with substituents on the six-membered ring, thus removing stereochemical factors. The difficulty of preparing benzotropones with electron-withdrawing groups in the benzene ring led us to synthesize four pyrido[*b*]- and pyrido[*c*]-tropones. These syntheses and the behaviour of the annelated tropones obtained under irradiation are described here.

Our first objective was the syntheses of the methoxybenzotropones (**12**), (**14**), and (**36**). The easiest to obtain was 2-methoxybenzotropone (**12**). The tetrahydro derivative (**9**) was synthesized as shown in Scheme 1, *via* the intermediates (**5**)—(**8**), and brominated with molecular bromine to give a mixture of dibromo (**10**) and tribromo (**11**) derivatives. Bromination by phenyltrimethylammonium tribromide (PTAT) gave only the dibromo derivative (**10**). Dehydrobromination of compound (**10**) by treatment with lithium chloride in boiling dimethylformamide (DMF) gave the 2-methoxybenzotropone (**12**). Similar dehydrobromination of the mixture of di- and tribromo derivatives gave compound (**12**) and a bromomethoxybenzotropone (**13**). The position of the bromine atom was established by the ^1H n.m.r. spectrum of compound (**13**). An ABX system with downfield signals at δ 7.9 and 7.25 and an upfield signal at δ6.55 having a major coupling (*J* 9 and 11 Hz) to both, indicates that the bromine atom is at C-6 or C-10. The presence of two downfield signals (β and δ to the carbonyl group) can only be accommodated by structure (**13**).

A similar route could not be used to prepare 1-methoxybenzotropone (**14**), because the pentanoic acid (**15**) fails to cyclize intramolecularly, giving instead a cyclophane by intermolecular cyclization.[7] Although a route to compound (**14**) exists[8] there is no yield recorded, and we chose to adopt the procedure of Scheme 1, aiming at the methyl derivative (**22**), with 2-methoxy-5-methylbenzaldehyde (**16**) as the starting material; we thus obtained the pentanoic acid (**19**) *via* compounds (**17**) and (**18**). Cyclization of the pentanoic acid was successful, polyphosphoric acid giving a 52% conversion into the benzocycloheptanone (**20**). Bromination by PTAT gave the dibromo derivative (**21**), which was dehydrobrominated to give 1-methoxy-4-methylbenzotropone (**22**).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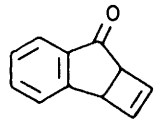
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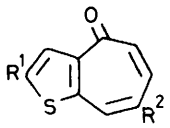
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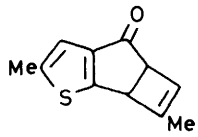
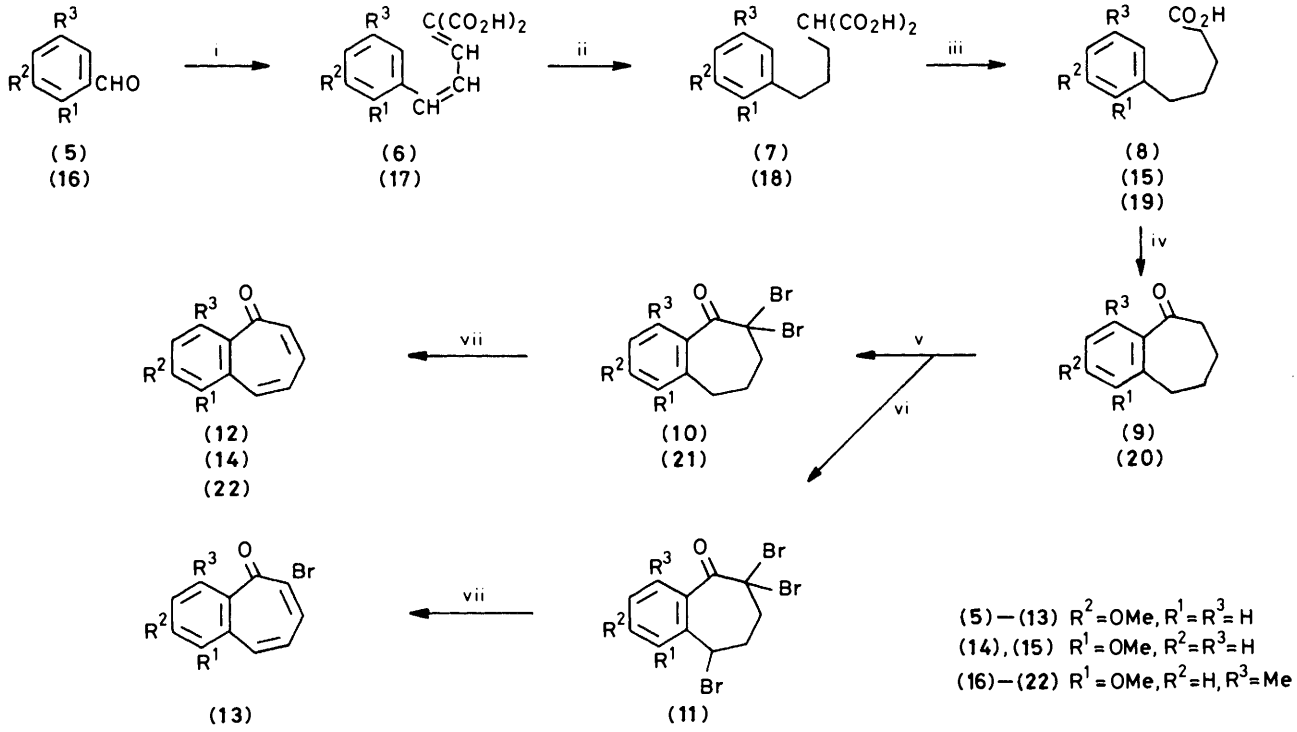

(4)

There is a report of the preparation of 3-methoxybenzotropone (**36**),[9] but the procedure produced a number of isomers, and the spectral evidence quoted does not identify with certainty the position of methoxy substitution. There are a number of reports of the preparation of the tetrahydro derivative (**28**);[10,11] we selected that of Smith and Berry,[12] outlined in Scheme 2, because we could thus obtain a range of 3-substituted benzotropones.

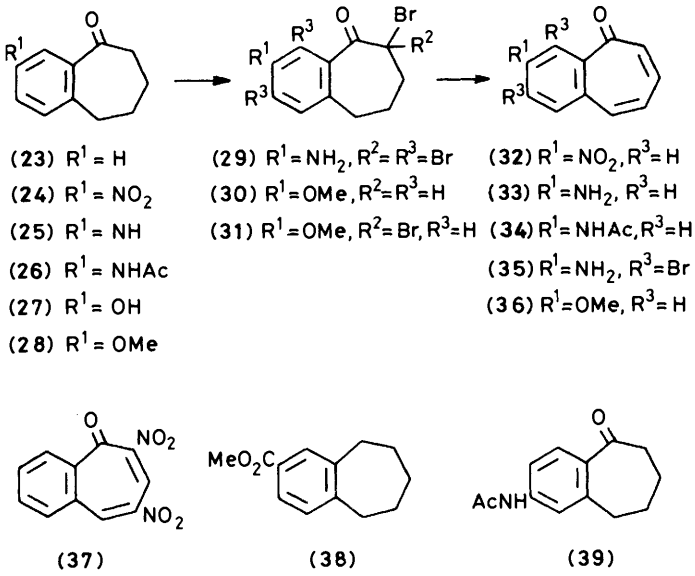
Thus, nitration of benzocycloheptanone (**23**) at low temperature gave the 3-nitro derivative (**24**), which could be converted into 3-nitrobenzotropone (**32**).[2] If the nitration temperature was allowed to rise, the major product was 2-(3-carboxypropyl)-5-nitrobenzoic acid. Transfer hydrogenation of the nitro compound (**32**) gave 3-aminobenzotropone (**33**), which was acetylated to give 3-acetylaminobenzotropone (**34**). The acetamide (**34**) could also be obtained by reduction of the nitro compound (**24**) to give amine (**25**), acetylation to give compound (**26**), and bromination and dehydrobromination.[2] An attempt to brominate the aminobenzocycloheptanone (**25**) gave a tetrabromo derivative (**29**), which on treatment with lithium chloride in DMF gave the dibromoaminobenzotropone (**35**). The amine (**25**) was diazotized and the diazonium salt solution heated to give the phenol (**27**); this was then methylated by sodium hydroxide with dimethyl sulphate to give the 3-methoxybenzocycloheptanone (**28**). Bromination of the methoxy derivative (**28**) using PTAT gave a mixture of monobromo- (**30**) and dibromo-methoxybenzocycloheptanone (**31**). Dehydrobromination of the dibromo derivative (**31**) gave 3-methoxybenzotropone (**36**). The u.v. absorption pattern was sufficiently similar to that published to confirm the structure of the compound obtained by Srivastava and Dev.[9]

Direct nitration of benzotropone (**1**) gave the 6,8-dinitro derivative (**37**).[13] Additionally, the benzocycloheptane (**38**) and the benzocycloheptanone (**39**) were prepared; the former could not be oxidized to the benzocycloheptanone.

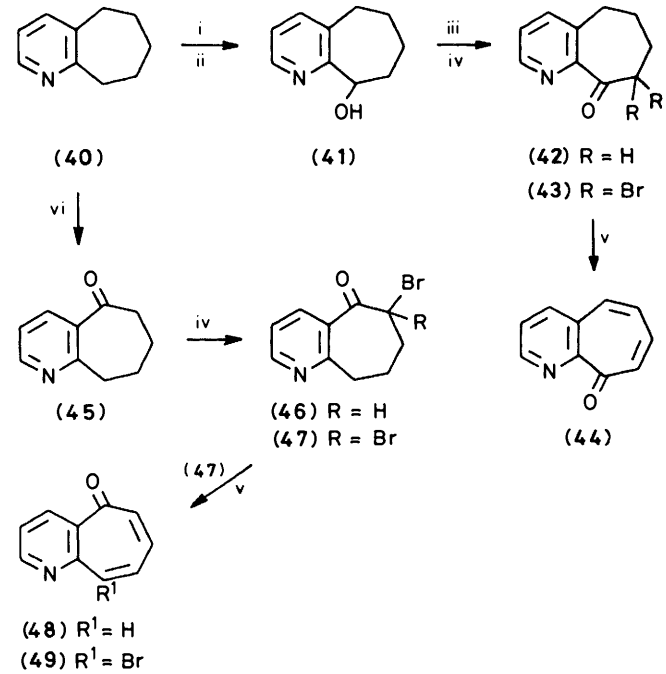
Difficulties associated with the synthesis of benzotropones



Scheme 1. *Reagents:* i, $CH_3CH{=}C(CO_2Et)_2$, $PhCH_2\overset{+}{N}Me_3OH^-$; ii, Pd/C, H_2; iii, Distil *in vacuo*; iv, PPA, 100 °C; v, $Ph\overset{+}{N}Me_3Br_3^-$, THF; vi, Br_2, CCl_4; vii, LiCl, DMF, boil



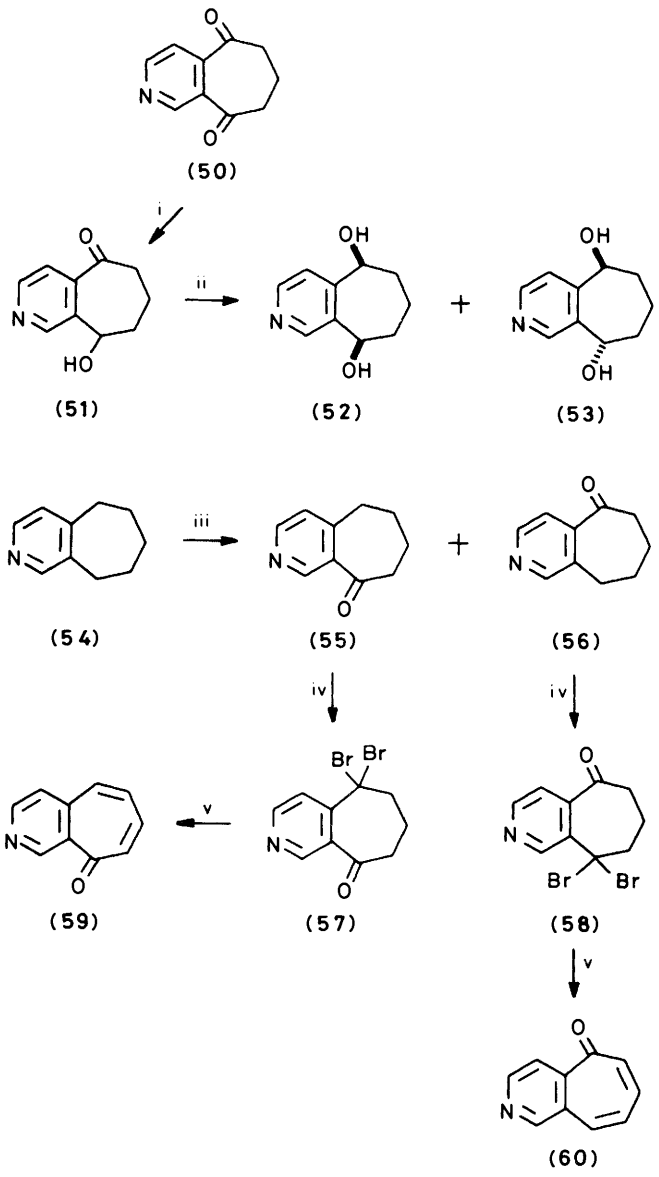
Scheme 2.



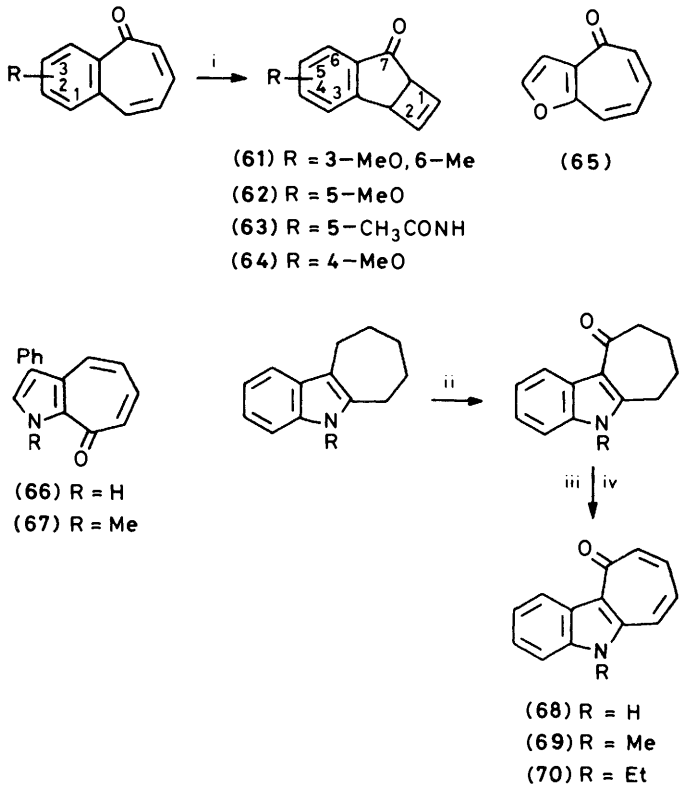
Scheme 3. *Reagents:* i, CH_3CO_2H, H_2O_2; ii, $(CH_3CO)_2O$; H^+, H_2O; iii, Me_2SO, $(CF_3CO)_2O$; iv, NBS; v, $LiCO_3$, DMF; vi, CrO_3, CH_3CO_2H, H_2SO_4

bearing electron-withdrawing groups led us to prepare the pyrido[*b*]tropones (**44**) and (**49**), and the pyrido[*c*]tropones (**59**) and (**60**). The pyrido[6]tropone (**44**) had been previously prepared[3] from cycloheptapyridine (**40**), but in very poor yield, by the route shown in Scheme 3. The weakest stage was the oxidation of the alcohol (**41**) to the ketone (**42**), performed in low yield by *N*-bromosuccinimide (NBS). No oxidation using metal ions was successful, but the dimethyl sulphoxide–trifluoroacetic anhydride reagent[14] gave the ketone in 83% yield. The bromination procedure to give compound (**43**) was also much improved by using NBS in place of PTAT.

The ketone (**45**) was made from the same starting material (**40**) by direct oxidation. Although the yield was modest, with recovery of some starting material, only one ketone was formed and the simplicity of the procedure makes it acceptable. Bromination of the ketone (**45**) by NBS gave a small amount of



Scheme 4. *Reagents:* i, $NaBH_4$ (1 equiv.); ii, $NaBH_4$, excess; iii, CrO_3, CH_3CO_2H, H_2SO_4; iv, NBS; v, Li_2CO_3, DMF



Scheme 5. *Reagents:* i, *h*V, MeOH; ii, DDQ, H_2O, THF; iii, $PhN^+Me_3Br_3^-$; iv, LiCl, DMF

the 6-bromoketone (**46**) and an excellent yield of the 6,6-dibromoketone (**47**). Dehydrobromination of the dibromoketone (**47**) in the usual way gave 5*H*-cyclohepta[*b*]pyridin-5-one (**48**). A small amount of a monobromopyridotropone was also isolated, and identified by its ^1H n.m.r. spectrum as the 9-bromo derivative (**49**). These reactions are summarized in Scheme 3.

An apparently versatile route to the two tropones (**59**) and (**60**) starts from the dione (**50**), which we have previously prepared.[15] We have made many attempts to functionalize one of the carbonyl groups selectively. We could not obtain a monohydrazone, a monotosylhydrazone, or a monosemicarbazone. The dione (**50**) failed to react with ethylene glycol to give a 1,3-dioxolane, even under forcing conditions, nor would it react with 2-ethyl-2-methyldioxolane in a transketalisation. Reduction using 1 equiv. of sodium borohydride gave a hydroxyketone. The evidence for the structure is not absolute, but the upfield shift of the signals due to 1-and 3-H in the hydroxyketone relative to those of the dione (**50**) lead us to favour the 9-hydroxy structure (**51**). All attempts to remove or to replace the hydroxy function in compound (**51**) failed. Reduction of the dione (**50**) with an excess of borohydride gave a compound with sharp m.p., with the correct analysis for a diol. However the ^1H n.m.r. spectrum showed two separate signals for each of 1-H and 3-H, integration showing a ratio of 2:1. The ^{13}C n.m.r. spectrum showed twice the expected number of peaks in the off-resonance spectrum, and hence we have probably two configurational isomers (**52**) and (**53**). We finally obtained the two pyridotropones (**59**) and (**60**) by oxidation of the cycloheptapyridine (**54**). The two ketones (**55**) and (**56**) were both obtained, in poor yield (12—15% of each) but, after separation, bromination to give the dibromoketones (**57**) and (**58**) was followed by dehydrobromination, giving the tropones (**59**) and (**60**). The structures of the two isomers are established by the ^1H n.m.r. spectra, where the signals due to 1-H and to 4-H are respectively deshielded by the adjacent carbonyl group.

Photochemistry.—The photochemical experiments showed very limited success; a theoretical study is to be published elsewhere. Irradiation was performed on methanolic solutions, with a medium pressure mercury lamp through Pyrex at ambient temperature. The only benzotropones which readily underwent electrocyclic reaction were those having electron-donating groups at position 1 or 3. Thus, the benzotropones (**22**), (**34**), and (**36**) gave the tricyclic compounds (**61**)—(**63**). The benzotropone (**12**) gave a small amount of the electrocyclic product (**64**), in approximately the same yield as that of compound (**2**) from the unsubstituted benzotropone (**1**). The tricyclic ketones were readily characterized by the n.m.r. spectra, which showed four characteristic signals, each integrating for one proton, at δ3.8, 4.3, 6.3, and 6.6 (2a-, 7a-, 1-, and 2-H) respectively. In the case of the methoxy substituted derivatives, the first signal was obscured by the Me singlet, but

addition of a small amount of $Eu(fod)_3$ reagent moved this signal downfield, indicating that $Eu(fod)_3$ complexes preferentially with the ketonic oxygen atom. All the other benzotropones gave, after prolonged irradiation, only polymeric materials. Similarly, the pyridotropones (**44**), (**48**), (**59**), and (**60**) gave no electrocyclic products, although a dimer of as yet undetermined structure was obtained from compound (**48**). It seems quite clear that benzotropone is at the lower limit of electrocyclization to give tricyclic ketones, any reduction in electron density being sufficient to inhibit the reaction. Mesomeric effects can be relayed in classical terms only from positions 1 and 3, giving an increased electron density at positions 6 and 8, the former being engaged in the bond forming process. A few tropones annelated with 'electron rich' heterocyclic rings have been prepared; these are furo[3,2-*b*]tropone (**65**),[3] the pyrrolotropone (**66**)[16] and its *N*-methyl derivative (**67**), and the three *N*-substituted indolotropones (**68**)—(**70**),[4b] of which the last is new. All, on irradiation, gave polymeric materials; it thus appears that only the previously examined thienotropones (**3**) have the necessary combination of increased electron density on the tropone ring and stability of the heteroaromatic ring to allow the production of non-polymeric photoproducts.

Experimental

M.p.s were determined on a Kofler heated stage, and are uncorrected. Chromatography was on columns of alumina (Woelm, activity shown thus – IV), silica (medium pressure), or on preparative plates (Merck silica P_F254). U.v. spectra were determined in 95% ethanol, i.r. spectra in chloroform, and n.m.r. spectra in $CDCl_3$, unless otherwise stated. Ether refers to diethyl ether.

3-*Methoxycinnamylidenemalonic Acid* (**6**).—This compound was prepared from 3-methoxybenzaldehyde and diethyl ethylidenemalonate[17] by the reported procedure,[18] m.p. 201—202 °C (lit.,[18] m.p. 201.6—202 °C); δ(CF_3CO_2H) 3.9 (3 H, s), 6.88—8.45 (7 H, m), and 11.8br (2 H, s, CO_2H).

5-(3-*Methoxyphenyl*)*pentane*-1,1-*dioic Acid* (**7**).—This compound was prepared as reported[18] by reduction of the acid (**6**), in virtually quantitative yield; δ 1.6—2.2 (4 H, m), 2.5—2.7 (2 H, t), 3.3—3.7 (1 H, t), 3.72 (3 H, s), 6.6—7.35 (4 H, m), and 10.2 br (2 H, s).

5-(3-*Methoxyphenyl*)*pentanoic Acid* (**8**).—This compound was prepared by decarboxylation of the acid (**7**) (80%), b.p. 142—143 °C/0.17 mmHg (lit.,[10] b.p. 200—220 °C/1 mmHg); δ 1.6—1.8 (4 H, m), 2.2—2.8 (4 H, m), 3.72 (3 H, s), 6.7—7.3 (4 H, m), and 9.5 br (1 H, s).

2-*Methoxy*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-5-*one* (**9**).—The acid (**8**) (15.8 g) was added in small portions during 1.25 h to a previously prepared homogeneous mixture of phosphorus pentaoxide (61.7 g) and 85% orthophosphoric acid (39.5 ml) at 100 °C. The vigorously stirred mixture was heated at 100 °C (6 h), poured onto ice–water, and extracted with ether (3 × 100 ml). The ether solution was washed with aqueous sodium hydroxide (5%) and water, dried ($MgSO_4$), filtered and evaporated. Distillation of the residue gave the cycloheptenone (**9**) (13.4 g, 94%), m.p. 57—58 °C (lit.,[10] m.p. 62 °C); δ 1.4—2 (4 H, m), 2.2—3.0 (4 H, m), 3.75 (3 H, s), 6.54—6.78 (2 H, m, 1- and 3-H), and 7.54—7.7 (1 H, d, *J* 9 Hz, 4-H).

6,6-*Dibromo*-2-*methoxy*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-5-*one* (**10**) *and* 6,6,9-*Tribromo*-2-*methoxy*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-5-*one* (**11**).—(*a*) PTAT (3.75 g) was added in ten portions at 10 min intervals to a stirred solution of the methoxybenzocycloheptanone (**9**) (1 g) in anhydrous tetrahydrofuran (THF) (100 ml) at room temperature. The mixture was stirred (24 h), a few drops of acetone added, and the filtered solution was evaporated. The residual oil solidified on trituration with light petroleum; recrystallization from methanol gave the *dibromo compound* (**10**), m.p. 82.5—83 °C (1.17 g, 62%) (Found: C, 41.75; H, 3.45. $C_{12}H_{12}Br_2O_2$ requires C, 41.4; H, 3.5%); $\nu_{max.}$ 1 680, 1 600, and 1 100 cm^{-1}; δ 1.6—2.2 (4 H, m), 2.6—2.9 (2 H, t, CH_2CBr_2), 3.8 (3 H, s), 6.5—6.8 (2 H, m, 1- and 3-H), and 7.36 (1 H, d, *J* 9 Hz, 4-H).

(*b*) Bromine (6.4 g) in carbon tetrachloride (15 ml) was added dropwise to a stirred solution of the methoxybenzocycloheptenone (**9**) (3.8 g) in CCl_4 (50 ml). The solution was boiled (1 h) and evaporated, giving a mixture (7.4 g). A sample, separated by p.l.c., contained the dibromoketone (**10**), and the *tribromoketone* (**11**), m.p. 75—76.5 °C (Found: C, 34.05; H, 2.6. $C_{12}H_{11}Br_3O_2$ requires C, 33.7; H, 2.6%); δ 1.58—2.2 (2 H, m), 2.6—2.9 (2 H, t, CH_2CBr_2), 3.8 (3 H, s), 5.1—5.3 (1 H, m, CHBr), 6.5—6.8 (2 H, m, 1- and 3-H), and 7.37 (1 H, d, *J* 9 Hz, 4-H).

2-*Methoxy*-5H-*benzocyclohepten*-5-*one* (**12**) *and* 6-*Bromo*-2-*methoxy*-5H-*benzocyclohepten*-5-*one* (**13**).—(*a*) The mixture obtained from experiment (*b*) above (7.3 g), with lithium chloride (3.65 g) was dissolved in dry DMF (450 ml) and the solution boiled and stirred under nitrogen (3 h). Removal of the solvent (oil pump) was followed by addition of water and extraction with ether. The ethereal extracts were dried ($MgSO_4$) and the filtered solution evaporated. The residual brown oil was distilled at 170—180 °C/0.2 mmHg, and the distillate separated by p.l.c. (multiple elution; ethyl acetate–toluene, 1:9). The slower running material was recrystallized from methanol to give the methoxybenzotropone (**12**) (2.62 g), m.p. 65.5—66.0 °C (lit.,[8] m.p. 73—74 °C) (Found: C, 77.6; H, 5.4. Calc. for $C_{12}H_{10}O_2$: C, 77.4; H, 5.4%). The faster running band was the *bromomethoxybenzotropone* (**13**), m.p. 156—157 °C, from methanol (1.15 g) (Found: C, 54.25; H, 3.4. $C_{12}H_9BrO_2$ requires C, 54.35; H, 3.5%); δ 3.94 (3 H, s), 6.4—6.6 (1 H, dd, *J* 9 and 11.7 Hz, 8-H), 7.04 (1 H, d, 1-H), 7.2—7.32 (1 H, dd, *J* 9 and 2.5 Hz, 3-H), 7.25—7.35 (1 H, dd, *J* 11.7 and 0.7 Hz, 9-H), 7.85—7.95 (1 H, dd, *J* 9 and 0.7 Hz), and 8.45—8.55 (1 H, d, *J* 9 Hz, 4-H).

(*b*) A similar experiment on the pure dibromo derivative (**10**) gave pure methoxybenzotropone (**12**).

2-*Methoxy*-5-*methylcinnamylidenemalonic Acid* (**17**).—A solution of 2-methoxy-5-methylbenzaldehyde[19] (14.6 g) and diethyl ethylidenemalonate (36.6 g), with benzyltrimethylammonium hydroxide (70 g) in methanol (165 ml) was kept at room temperature (48 h). The solution was diluted with water (500 ml), boiled (2 h), and then cooled and acidified using 5M-hydrochloric acid. After 24 h at 5 °C, yellow crystals formed and these were filtered off. Recrystallization from benzene–ethyl acetate gave the *cinnamylidenemalonic acid* (**17**), m.p. 140 °C (20 g, 76%) (Found: C, 60.35; H, 6.15. $C_{14}H_{14}O_5 \cdot H_2O$ requires C, 60.05; H, 5.75%); δ([$^2H_6$]acetone) 2.28 (3 H, s), 3.88 (3 H, s), 6.75—8.1 (6 H, m), and 9.38 (2 H, s).

5-(2-*Methoxy*-5-*methylphenyl*)*pentane*-1,1-*dioic Acid* (**18**) *and* 5-(2-*Methoxy*-5-*methylphenyl*)*pentanoic Acid* (**19**).—(*a*) A solution of the malonic acid (**17**) (20 g) in 95% ethanol (1 l) was hydrogenated at ambient temperature and pressure, using palladium on charcoal (10%, 1.5 g) until absorption ceased. Filtration and evaporation of the filtrate gave virtually pure pentanedioic acid (**18**) (20.3 g, quant.); δ 1.55—2.2 (4 H, m), 2.3 (3 H, s), 2.4—2.75 (2 H, m), 3.3—4.75 (1 H, m), 3.75 (3 H, s), 6.4—7.2 (3 H, m), and 10.3 br (2 H, m).

(*b*) The crude acid (**18**) (20.1 g) was heated *in vacuo*, when the *pentanoic acid* (**19**) distilled off, b.p. 160 °C/0.05 mmHg, m.p.

47.5—48 °C (15.2 g, 91%) (Found: C, 70.35; H, 8.15. $C_{13}H_{18}O_3$ requires C, 70.25; H, 8.1%); $\nu_{max.}$ 1 710, 1 600 cm^{-1}; δ 1.55—1.85 (4 H, m), 2.2 (3 H, s), 2.3—2.7 (4 H, m), 3.7 (3 H, s), 6.0—7.1 (3 H, m), and 9.0 (1 H, s).

1-*Methoxy*-4-*methyl*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-5-*one* (**20**).—The pentanoic acid (**19**) (4.2 g) was added in five portions during 1 h to polyphosphoric acid at 100 °C [freshly prepared from P_2O_5 (20.6 g) and 85% H_3PO_4 (13 ml)]. The solution was heated at 100 °C (5 h) and worked up as described for compound (**9**), but the crude product was purified by chromatography on alumina (150 g; IV), eluting with benzene–light petroleum (1:4). The *benzocycloheptenone* (**20**) was a yellow liquid (2 g, 52%) (Found: C, 76.25; H, 7.6. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.9%); $\nu_{max.}$(neat liquid) 1 688, 1 594, 1 580, 1 480, 1 190, and 1 050 cm^{-1}; δ 1.5—1.9 (4 H, m), 2.2 (3 H, s), 2.4—3.9 (4 H, m), 3.7 (3 H, s), 6.7 (1 H, d, *J* 8.4 Hz), and 6.9 (1 H, d, *J* 8.4 Hz).

6,6-*Dibromo*-1-*methoxy*-4-*methyl*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-5-*one* (**21**).—The procedure (*a*) used to prepare compound (**10**) gave a mixture, seen from the ^{1}H n.m.r. spectrum to contain some monobromoketone. The process was repeated to give a gum which was purified on alumina (200 g; IV), eluting with benzene–light petroleum (2:3). The *dibromoketone* (**21**), crystallized from chloroform–light petroleum, had m.p. 73—74 °C (3.09 g, 98%) (Found: C, 43.1; H, 3.8. $C_{13}H_{14}Br_2O_2$ requires C, 43.1; H, 3.9%); $\nu_{max.}$(Nujol) 1 716, 1 605, 1 585, 1 480, 1 275, and 975 cm^{-1}; δ 1.6—2.0 (2 H, m), 2.2 (3 H, s), 2.4—2.7 (2 H, m), 3.2—3.5 (2 H, m), 3.7. (3 H, s), 6.75 (1 H, d, *J* 8.4 Hz), and 7.0 (1 H, d, *J* 8.4 Hz).

1-*Methoxy*-4-*methyl*-5H-*benzocyclohepten*-5-*one* (**22**).—A mixture of the dibromoketone (**21**) (3 g) and anhydrous lithium chloride in anhydrous DMF (300 ml) was boiled and stirred under nitrogen (4 h). Evaporation, treatment with water and chloroform, and evaporation of the dried ($MgSO_4$) chloroform solution gave the crude product. Purification by p.l.c. (ethyl acetate–toluene, 1:9) gave the pure 1-*methoxy*-4-*methylbenzotropone* (**22**) (1.4 g, 83%) (Found: C, 77.65; H, 6.2. $C_{13}H_{12}O_2$ requires C, 77.95; H, 6.05%); $\nu_{max.}$ 1 650, 1 620, 1 590, and 1 468 cm^{-1}; δ 2.4 (3 H, s), 3.86 (3 H, s), 6.5—6.8 (3 H, m, 6-, 7-, 8-H), 6.9 (1 H, d, *J* 8.4 Hz, 2-H), 7.3 (1 H, d, *J* 8.4 Hz, 3-H), and 7.9 (1 H, d, *J* 11.8 Hz, 9-H).

3-*Nitro*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-5-*one* (**24**) *and* 2-(3-*Carboxypropyl*)-5-*nitrobenzoic Acid*.—Nitration as described[11] gave the nitrobenzocycloheptenone (**24**) as colourless crystals, m.p. 92—93 °C in 85% yield. If the temperature was allowed to rise during the nitration, the product was the *dicarboxylic acid*, m.p. 122—123 °C from water (63%) (Found: C, 52.25; H, 4.3; N, 5.9. $C_{11}H_{11}NO_6$ requires C, 52.15; H, 4.35; N, 5.55%); δ 1.8—2.15 (2 H, m), 2.55—3.1 (4 H, m), 7.25 (1 H, d, *J* 8 Hz, 3-H), 8.1 (1 H, dd, *J* 8 and 2 Hz, 4-H), 8.4 (1 H, d, *J* 8 Hz, 6-H), and 10.0 (2 H, s).

3-*Amino*-5H-*benzocyclohepten*-5-*one* (**33**).—A mixture of cyclohexene (8.2 g), palladium on charcoal (0.5 g, 10%), and the nitrobenzotropone (**32**)[2] (2 g) in 45% ethanol (350 ml) was boiled vigorously under reflux (15 h). Filtration and evaporation of the filtrate gave crude amine, which was purified by recrystallization from absolute ethanol to give the 3-*aminobenzotropone* (**33**), m.p. 150—152 °C (1.35 g, 79%) (Found: C, 77.0; H, 5.15; N, 8.3. $C_{11}H_9NO$ requires C, 77.2; H, 5.25; N, 8.2%); $\nu_{max.}$(Nujol) 3 430, 3 350, 1 660, 1 615, 1 570, and 1 520 cm^{-1}; $\lambda_{max.}$ 243, 268, 360, and 434 nm ($\log_{10}\varepsilon$ 4.28, 4.4, 4.06, and 3.84); δ 4.0br (2 H, s, NH_2), 6.2—7.25 (5 H, m), 7.45 (1 H, d, *J* 8.5 Hz, 1-H), and 7.75 (1 H, d, *J* 3.2 Hz, 4-H). Treatment of the amine (**33**), in pyridine solution, with acetyl chloride gave the *N*-acetyl derivative (**34**), m.p. 214—215 °C, identical with that previously prepared.[2]

3-*Amino*-2,4-*dibromo*-5H-*benzocyclohepten*-5-*one* (**35**).—(*a*) A solution of bromine (6.4 g) in carbon tetrachloride (20 ml) was added dropwise to a solution of the amine (**25**) (1.75 g) in carbon tetrachloride (100 ml), and stirring continued (12 h). Evaporation of the solvent gave a brown oil, treated with aqueous sodium hydrogen carbonate and dichloromethane. The organic layer was dried, evaporated, and distilled (bulb tube) to give the tetrabromo derivative (**29**) as a brown oil, δ 1.7—2.1 (2 H, m), 2.35—2.8 (4 H, m), 4.72 br (2 H, s, NH_2), and 7.1 (1 H, s, 1-H).

(*b*) A solution of the crude tetrabromo derivative (**29**) (3.5 g), with anhydrous lithium chloride (1.9 g) in anhydrous DMF (150 ml), was boiled and stirred under nitrogen (6 h). Work up as described for compound (**12**), followed by chromatography on alumina (200 g; IV), eluting with ethyl acetate–light petroleum (1:9) gave the *dibromoamine* (**35**) (0.94 g, 41%), m.p. 78—79 °C from methanol (Found: C, 39.45; H, 2.25; N, 4.2. $C_{11}H_7Br_2NO$ requires C, 40.1; H, 2.1; N, 4.25%); δ 5.2 br (2 H, s, NH_2), 6.3—6.6 (1 H, m, 8-H), 6.75—6.85 (2 H, m), 6.95—7.05 (1 H, dd, 9-H), and 7.7 (1 H, s, 1-H).

4-(3-*Aminophenyl*)*butane*-1,1-*dioic Acid*.—(*a*) Using the procedure described for compound (**17**), 3-nitrocinnamylidenemalonic acid was obtained from 3-nitrobenzaldehyde (22.65 g), m.p. 156 °C (31.5 g, 80%).

(*b*) Hydrogenation as described for compound (**17**), gave from 3-nitrocinnamylidenemalonic acid (13.5 g), the *aminophenylbutanedioic acid*, m.p. 146—147 °C (12.3 g, 92%) (Found: C, 60.75; H, 6.45; N, 6.0. $C_{12}H_{15}NO_4$ requires C, 60.75; H, 6.35; N, 5.9%); δ [$(CD_3)_2SO$] 1.4—1.8 (4 H, m), 2.0br (3 H, s, NH_3^+), 2.3—2.6 (2 H, m), 3.4—3.7 (1 H, m), 6.2—7.0 (4 H, m), and 8.7 (1 H, s, CO_2H).

5-(3-*Acetamidophenyl*)*pentanoic Acid*.—Decarboxylation of the aminophenylbutanedioic acid gave crude 5-(3-aminophenyl)pentanoic acid, acetylated to give 5-(3-acetamidophenyl)pentanoic acid, m.p. 137—138 °C (68%) (lit.,[20] m.p. 138—139 °C). Cyclization as reported[20] gave the acetamidobenzocycloheptanone (**39**) in 56% yield.

6-*Bromo*-3-*methoxy*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-5-*one* (**30**) *and* 6,6-*Dibromo*-3-*methoxy*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-5-*one* (**31**).—A stirred solution of the methoxy compound (**28**) (1.3 g) in THF (50 ml) was treated with PTAT (7 g) during several hours, and the mixture stirred overnight. After addition of a few drops of acetone, the filtered solution was evaporated. An n.m.r. spectrum of the crude product showed a monobrominated derivative to be present. Separation of the mixture on a Chromatotron (light petroleum as eluant) gave the two pure products. The *monobromo derivative* (**30**) had b.p. 130 °C/0.05 mmHg (bulb tube) (Found: C, 53.2; H, 5.0. $C_{12}H_{13}BrO_2$ requires, C, 53.55; H, 4.85%); δ 1.7—2.6 (4 H, m), 2.7—3.0 (2 H, m), 3.8 (3 H, s, OCH_3), 4.7—5.0 (1 H, dd, CHBr), and 6.8—7.3 (3 H, m, 1-, 2-, and 4-H). The *dibromo derivative* (**31**), had b.p. 140 °C/0.05 mmHg (bulb tube) (1.5 g, 63%) (Found: C, 41.4; H, 3.45. $C_{12}H_{12}Br_2O_2$ requires C, 41.4; H, 3.45%); δ 1.7—2.2 (2 H, m), 2.5—3.0 (4 H, m), 3.8 (3 H, s, OCH_3), and 6.9—7.2 (3 H, m); *m/z* 344, 346, and 348 (M^+).

3-*Methoxy*-5H-*benzocyclohepten*-5-*one* (**36**).—Dehydrobromination using lithium carbonate (1 g) and the dibromoketone (**31**) (1 g) in DMF (50 ml) gave, after work-up, an oil, separated on a Chromatotron (eluant ethyl acetate–light petroleum, 1:9) to give the 3-*methoxybenzotropone*, b.p. 105—

110 °C/0.05 mmHg (bulb tube) (0.49 g, 91%), δ 6.5—6.7 (1 H, ddd, *J* 11.3, 7.0, and 2.2 Hz, 8-H), 7.0—7.1 (2 H, m, 6-, 7-H), 7.2—7.3 (1 H, dd, *J* 8.6 and 3 Hz, 2-H), 7.25—7.35 (1 H, d, *J* 11.3 Hz, 9-H), 7.6 (1 H, d, *J* 8.6 Hz, 1-H), and 8.0 (1 H, d, *J* 3 Hz, 4-H). From [$^2H_6$]benzene, $J_{6,7}$ 12.1, $J_{6,8}$ 1.2 Hz.

5,6,7,8-*Tetrahydro*-9H-*cyclohepta*[b]*pyridin*-9-*one* (**42**).—Anhydrous dichloromethane (30 ml) and anhydrous dimethyl sulphoxide (4.3 ml) were cooled to −70 °C, and trifluoroacetic anhydride (6.4 ml) in dichloromethane (15 ml) was added dropwise during 15 min. After a further 10 min stirring at −70 °C, a solution of the alcohol (**41**) (4.9 g) in dichloromethane (20 ml) was added dropwise (10 min, then 30 min). Dry triethylamine (13 ml) was added dropwise, and the mixture allowed to come to room temperature. Removal of the solvent and chromatography on alumina (IV) gave the ketone (**42**), b.p. 91 °C/0.1 mmHg (4.05 g, 83%), identical with that previously prepared.[3]

8,8-*Dibromo*-6,7,8,9-*tetrahydro*-9H-*cyclohepta*[b]*pyridin*-9-*one* (**43**).—A solution of recrystallized and dried *N*-bromosuccinimide (9.5 g) and benzoyl peroxide (0.12 g) was added to a solution of the ketone (**42**) (4.3 g) in carbon tetrachloride (100 ml), and the mixture boiled over a 150-W bulb until the reaction was complete (t.l.c.). The cooled solution was filtered, washed with aqueous sodium hydrogen carbonate, then water, and dried ($MgSO_4$). Evaporation of the solvent gave the dibromoketone (**43**), recrystallized from methanol, m.p. 82—84 °C (lit.,[3] m.p. 83—84 °C) (6.5 g, 78%; lit.,[3] yield 14%).

6,7,8,9-*Tetrahydro*-5H-*cyclohepta*[b]*pyridin*-5-*one* (**45**).—A solution of chromium trioxide (5.3 g) in water (3 ml) and acetic acid (15 ml) was added at 5—10 °C to a solution of tetrahydrocyclohepta[*b*]pyridine (**40**) (5 g) in a mixture of acetic acid (27 ml) and concentrated sulphuric acid (5.5 ml), and the mixture stirred overnight. Evaporation of the acetic acid under reduced pressure, basification of the residue with aqueous sodium hydrogen carbonate, and extraction with dichloromethane gave, after drying and evaporation, a residue, chromatographed on silica (medium pressure, eluted with ethyl acetate–light petroleum, 1:4). Two fractions were obtained, fraction one being tetrahydrocyclohepta[*b*]pyridine (**40**) (1.8 g, 36% recovery) and the second the tetrahydrocycloheptapyridin-5-one (**45**) (0.8 g, 18%), b.p. 80—81 °C/0.2 mmHg (lit.,[21] b.p. 135 °C/10 mmHg).

6-*Bromo*- (**46**) *and* 6,6-*Dibromo*-6,7,8,9-*tetrahydro*-5H-*cyclohepta*[b]*pyridin*-5-*one* (**47**).—A solution of the ketone (**45**) (3.29 g) in carbon tetrachloride (125 ml), with NBS (7.24 g) and azobisisobutyronitrile (0.3 g) was boiled under nitrogen until t.l.c. showed no starting material. The cooled solution was filtered, washed with aqueous sodium hydrogen carbonate then water, dried, filtered, and evaporated. Chromatography on silica, eluting with dichloromethane, gave two fractions. The first fraction was the 6-*bromo derivative* (**46**), further purified by p.l.c. (0.3 g, 6%) (Found: C, 49.6; H, 4.1; N, 5.65. $C_{10}H_{10}BrNO$ requires C, 50.0; H. 4.2; N, 5.85%); $\nu_{max.}$ 1 700 cm^{-1}; δ 2.44 (4 H, m), 2.6—3.41 (2 H, m), 5.64 (1 H, m, CHBr), 7.33 (1 H, dd, *J* 4.7 and 7.8 Hz, 3-H), 7.94 (1 H, dd, *J* 7.8 and 1.8 Hz, 4-H), and 8.62 (1 H, dd, *J* 4.7 and 1.8 Hz, 2-H). *m/z* 239, 241 (M^+). Fraction 2 was the 6,6-*dibromo derivative* (**47**) (6 g, 91%) m.p. 111.5—112.0 °C (from ethanol) (Found: C, 37.4; H, 2.8; N, 4.4. $C_{10}H_9Br_2NO$ requires C, 37.65; H, 2.85; N, 4.4%); $\nu_{max.}$ 1 700 cm^{-1}; δ 2.23 (2 H, m), 3.02 (4 H, m), 7.34 (1 H, dd, *J* 4.6 and 7.8 Hz, 3-H), 7.82 (1 H, dd, *J* 7.8 and 1.8 Hz, 4-H), 8.83 (1 H, dd, *J* 4.6 and 1.8 Hz, 2-H); *m/z* 317, 319, and 321 (M^+).

5H-*Cyclohepta*[b]*pyridin*-5-*one* (**48**).—A mixture of the dibromoketone (**47**) (4.0 g) and lithium carbonate (3 g) in dimethylformamide (500 ml) was stirred and boiled under nitrogen (5 h). The cooled solution was filtered, the solvent removed under reduced pressure, and the residue separated by p.l.c. (ethyl acetate) to give two products. The major product was the *cycloheptapyridin*-5-*one* (**48**), m.p. 85—86 °C (1.02 g, 51%) (Found: C, 76.05; H, 4.4; N. 8.9. $C_{10}H_7NO$ requires C, 76.4; H, 4.5; N, 8.9%); $\lambda_{max.}$ 217.5, 240, 247.5, 302.5, 340, and 351 nm ($\log_{10}\varepsilon$ 4.52, 4.16, 4.15, 3.72, 3.78, and 3.73); $\nu_{max.}$ 1 640, 1 605, and 1 580 cm^{-1}; δ 6.92 (1 H, ddd, *J* 6.9, 10.5, and 2.4 Hz), 7.07 (2 H, m, 6-, 7-H), 7.55 (1 H, dd, *J* 8.3 and 4.4 Hz, 3-H), 7.67 (1 H, dd, *J* 10.5 Hz, 9-H), 8.75 (1 H, dd, *J* 8.3 and 1.8 Hz), and 8.98 (1 H, dd, *J* 4.4 and 1.8 Hz, 2-H). The minor fraction was the 9-*bromocycloheptapyridinone* (**49**), m.p. 118—118.5 °C (0.25 g, 7.5%) (Found: C, 51.1; H, 2.5; N, 5.65. $C_{10}H_6BrNO$ requires C, 50.9; H, 2.55; N, 5.95%); $\lambda_{max.}$ 206, 220, 259sh, 263sh, 342.5, and 350sh nm ($\log_{10}\varepsilon$ 4.44, 4.5, —, —, 3.84, —); δ 6.95 (2 H, m, *J* 8.5 and 11.9 Hz, 6-, 7-H), 7.6 (1 H, dd, *J* 8.1 and 4.4 Hz, 3-H), 7.76 (1 H, dd, *J* 8.5 and 1.2 Hz, 8-H), 8.6 (1 H, dd, *J* 8.1 and 1.8 Hz, 4-H), and 9.06 (1 H, dd, *J* 4.4 and 1.8 Hz, 2-H); *m/z* 235, 237 (M^+).

9-*Hydroxy*-6,7,8,9-*tetrahydro*-5H-*cyclohepta*[c]*pyridin*-5-*one* (**51**).—To a stirred solution of the dione (**50**) (1 g) in ethanol (20 ml), sodium borohydride was added (54 mg), and the solution stirred till t.l.c. showed no starting material. Filtration, evaporation, and p.l.c. purification of the residue (ethyl acetate–methanol, 95:5) gave the *hydroxy ketone* (**51**), m.p. 124.5—125.5 °C (from ether) (0.57 g, 58%) (Found: C, 67.8; H, 6.3; N, 7.65. $C_{10}H_{11}NO_2$ requires C, 67.8; H, 6.25; N, 7.9%); $\lambda_{max.}$ 239sh, 251, 257, 303sh ($\log_{10}\varepsilon$ —, 3.46, 3.43, —); $\nu_{max.}$ (KBr) 3 370, 1 690, and 1 595 cm^{-1}; δ 1.84 (4 H, m), 2.73 (2 H, m), 4.74 br (1 H, s, OH), 5.0 (1 H, m, CHOH), 7.48 (1 H, d, J 5 Hz, 4-H), 8.52 (1 H, d, J 5 Hz, 3-H), and 8.59 (1 H, s, 1-H).

5,9-*Dihydroxy*-6,7,8,9-*tetrahydro*-5H-*cyclohepta*[c]*pyridines* (**52**) *and* (**53**).—Repetition of the borohydride reduction using 2 equiv. of borohydride gave the *diols* (**52**) and (**53**) (60%), m.p. 127.5—128.5 °C (from acetonitrile) (Found: C, 67.25; H, 7.5; N, 7.8. $C_{10}H_{13}NO_2$ requires C, 67.0; H, 7.3; N, 7.8%); $\nu_{max.}$(KBr) 3 350 cm^{-1}. The ^1H n.m.r. spectrum showed multiplets at δ 1.84 (6 H), 5.29 (4 H) and two sets of signals in the pyridine CH region roughly in the ratio 2:1. ^{13}C N.m.r. confirmed the presence of two isomers, with 20 signals in the fully decoupled spectrum. No firm decision was reached regarding the conformational and configurational isomerism.

Oxidation of 6,7,8,9-*Tetrahydro*-5H-*cyclohepta*[c]*pyridine* (**54**).—Oxidation of the tetrahydrocyclohepta[*c*]pyridine (**54**) was carried out as described for the isomer (**40**) on six batches, each of 5 g. Separation of the bulked products by medium pressure chromatography, eluting with ethyl acetate–light petroleum (1:4) gave three main fractions. Fraction 1 was unchanged starting material (9.9 g, 33%). Fraction 2 was 5,6,7,8-*tetrahydro*-9H-*cyclohepta*[c]*pyridin*-9-*one* (**55**), b.p. 106 °C/0.3 mmHg (4 g, 12%). The *picrate* had m.p. 162—163 °C (from ethanol) (Found: C, 49.1; H, 3.65; N, 14.35. $C_{16}H_{14}N_4O_8$ requires C, 49.25; H, 3.6; N, 14.35%); $\nu_{max.}$ 1 700 cm^{-1}; δ 1.85 (4 H, m), 2.8 (4 H, m), 7.05 (1 H, d, *J* 5 Hz, 4-H), 8.45 (1 H, d, *J* 5 Hz, 3-H), and 8.7 (1 H, s). Fraction 3 was 6,7,8,9-*tetrahydro*-5H-*cyclohepta*[c]*pyridin*-5-*one* (**56**) (5.1 g, 15.4%), b.p. 95 °C/0.015 mmHg; *picrate*, m.p. 140—141 °C (from ethanol) (Found: C, 48.95; H, 3.6; N, 14.5%); $\nu_{max.}$ 1 698 cm^{-1}; δ 2.9 (4 H, m), 2.75 (4 H, m), 7.4 (1 H, d, *J* 5 Hz, 4-H), 8.45 (1 H, s), and 8.5 (1 H, d, *J* 5 Hz, 3-H).

5,5-*Dibromo*-5,6,7,8-*tetrahydro*-9H-*cyclohepta*[c]*pyridin*-9-*one* (**57**).—Bromination by NBS of compound (**55**) as described

for compound (**45**) gave, after p.l.c. (ethyl acetate–light petroleum, 1:4), the *dibromo ketone* (**57**); *picrate*, m.p. 149—150 °C (ethanol) (Found: C, 35.05; H, 2.5; N, 10.15. $C_{16}H_{12}Br_2N_4O_8$ requires C, 35.05; H, 2.2; N, 10.2%). The free base (**57**) had $\nu_{max.}$ 1 715 cm^{-1}; δ 2.15 (2 H, m), 3.0 (4 H, m), 7.95 (1 H, d, *J* 6 Hz, 4-H), 8.45 (1 H, s, 1-H), and 8.6 (1 H, d, *J* 6 Hz, 3-H); *m/z* 317, 319, and 321 (M^+).

9,9-*Dibromo*-6,7,8,9-*tetrahydro*-5H-*cyclohepta*[c]*pyridin*-5-*one* (**58**).—Prepared as described above from compound (**56**) in 34% yield, the *dibromo ketone* (**58**) *picrate* had m.p. 135—136 °C (ethanol) (Found: C, 35.5; H, 2.15; N, 10.3%). The free base (**58**) had $\nu_{max.}$ 1 710 cm^{-1}; δ 2.1 (4 H, m), 2.85 (4 H, m), 7.0 (1 H, d, *J* 5 Hz, 4-H), 8.45 (1 H, d, *J* 5 Hz, 3-H), and 9.3 (1 H, s, 1-H).

9H-*Cyclohepta*[c]*pyridin*-9-*one* (**59**).—The dibromo ketone (**57**) (1.25 g) was heated in DMF (1 l) with lithium carbonate (1.25 g). Work-up as described for compound (**45**) gave, after p.l.c. (ethyl acetate–light petroleum, 1:4), the *pyridotropone* (**59**) *picrate* (0.4 g of base, 64%), m.p. 198—199 °C (ethanol) (Found: C, 49.65; H, 2.45; N, 13.95. $C_{16}H_{10}N_4O_8$ requires C, 49.75; H, 2.6; N, 14.5%); $\lambda_{max.}$ 214, 248, 315, and 345sh nm ($\log_{10}$ ε 4.36, 4.02, 3.83, —); $\nu_{max.}$ 1 647, 1 612, and 1 575 cm^{-1}; δ 6.87 (1 H, dd, *J* 10.5 and 6.3 Hz, 6-H), 7.03 (2 H, m, 7-, 8-H), 7.22 (1 H, dd, *J* 10.5 and 1.7 Hz, 5-H), 7.45 (1 H, d, *J* 5.1 Hz, 4-H), 8.84 (1 H, d, *J* 5.1 Hz, 3-H), and 9.57 (1 H, s, 1-H).

5H-*Cyclohepta*[c]*pyridin*-5-*one* (**60**).—Prepared as for compound (**58**) in 80% yield, the *pyridotropone* (**60**) *picrate* had m.p. 201—202 °C (ethanol) (Found: C, 49.7; H, 2.65; N, 13.95%). The free base (**60**) had $\lambda_{max.}$ 217, 244sh, 252sh, 312, 325, and 348 nm ($\log_{10}$ ε 4.45, —, —, 3.98, 3.98, 3.84); $\nu_{max.}$ 1 645, 1 620, and 1 585 cm^{-1}; δ 6.88 (1 H, ddd, *J* 7.3, 11.1, and 1.8 Hz, 8-H), 7.19 (2 H, m, 6-, 7-H), 7.39 (1 H, dd, *J* 11.1 and 1.3 Hz, 9-H), 8.24 (1 H, d, *J* 5.3 Hz, 4-H), 8.83 (1 H, d, *J* 5.3 Hz, 3-H), and 9.05 (1 H, s, 1-H).

General Procedure for Irradiation.—A solution of the tropone (0.6—1 g) in absolute methanol (750 ml) was degassed in a stream of nitrogen, then irradiated using a Hanovia medium-pressure mercury lamp through a Pyrex sleeve at ambient temperature. The progress of the reaction was checked by t.l.c., monitoring the disappearance of the starting material. When the reaction was complete, the methanol was evaporated and the residue triturated with ether, removing lower molecular weight products from any polymer. Evaporation of the ethereal solution was followed by p.l.c., using mixtures of ethyl acetate and toluene as the eluting solvents.

3-*Methoxy*-6-*methyl*-2a,7a-*dihydro*-7H-*cyclobut*[a]*inden*-7-*one* (**61**) was obtained as a solid (40%), m.p. 88—89 °C (Found: C, 77.8; H, 6.2. $C_{13}H_{12}O_2$ requires C, 77.95; H, 6.05%); $\nu_{max.}$ 1 700 cm^{-1}; δ 2.44 (3 H, s), 3.75 (4 H, m, OCH_3 and 2a-H), 4.2 (1 H, m, 7a-H), 6.2 (1 H, m, 1-H), 6.55 (1 H, m, 2-H), 6.8 (1 H, d, *J* 9 Hz, 4-H), and 7.0 (1 H, d, *J* 9 Hz, 5-H).

5-*Methoxy*-2a,7a-*dihydro*-7H-*cyclobut*[a]*inden*-7-*one* (**62**) was obtained as a solid (25%) after bulb tube distillation, b.p. 130 °C/0.5 mmHg (Found: C, 77.35; H, 5.6. $C_{12}H_{10}O_2$ requires C, 77.4; H, 5.4%); $\nu_{max.}$ 1 700 cm^{-1}; δ 3.7—3.9 (4 H, m, OCH_3 and 2a-H) 4.3 (1 H, m, 7a-H), 6.3 (1 H, m, 1-H), 6.6 (1 H, m, 2-H), and 7.0—7.4 (3 H, m, 3-, 4-, 6-H).

5-*Acetamido*-2a,7a-*dihydro*-7H-*cyclobut*[a]*inden*-7-*one* (**63**) was obtained as a solid (35%), m.p. 173—174 °C (Found: C, 73.1; H, 5.15; N, 6.75. $C_{13}H_{11}NO_2$ requires C, 73.25; H, 5.15; N, 6.55%); $\nu_{max.}$ 1 695, 1 615, and 1 595 cm^{-1}; δ 2.05 (3 H, s), 3.8 (1 H, m, 2a-H), 4.25 (1 H, m, 7a-H), 6.3 (1 H, m, 1-H), 6.55 (1 H, m, 2-H), 7.35 (1 H, d, *J* 8.3 Hz, 3-H), 7.75 (1 H, d, *J* 2.5 Hz, 6-H), 8.0 (1 H, dd, *J* 8.3 and 2.5 Hz, 4-H), and 9.0 br (1 H, s, NH).

4-*Methoxy*-2a,7a-*dihydro*-7H-*cyclobut*[a]*inden*-7-*one* (**64**) was isolated as an oil (8%) (Found: C, 77.3; H, 5.4. $C_{12}H_{10}O_2$ requires C, 77.4; H, 5.4%); δ 3.7—3.9 (4 H, m, OCH_3 and 2a-H), 4.25 (1 H, m, 7a-H), 6.3 (1 H, m, 1-H), 6.55 (1 H, m, 2-H), 6.75—6.95 (2 H, m, 3-, 5-H), and 7.6 (1 H, d, *J* 9 Hz, 6-H).

1-*Methyl*-3-*phenylcyclohepta*[b]*pyrrol*-8(1H)-*one* (**67**).—The pyrrolotropone (**66**) (0.22 g) in dimethoxyethane (30 ml) with methyl iodide (0.14 g) and sodium hydride (96 mgm) was boiled (20 h); a further quantity of methyl iodide was added and the mixture again boiled (40 h). The solvent was removed under reduced pressure, and water and chloroform added. The dried chloroform extracts were evaporated, and the residual gum purified by p.l.c. (ethyl acetate–toluene, 1:9). The N-*methyl derivative* had m.p. 109—110 °C (Found: C, 81.95; H, 5.75; N, 6.05. $C_{16}H_{13}NO$ requires C, 81.7; H, 5.55; N, 5.95%); $\nu_{max.}$(KBr) 1 618, 1 550, and 1 520 cm^{-1}; δ 6.3—6.6 (1 H, m, 5-H), 6.9—7.3 (8 H, m), and 7.45 (1 H, d, *J* 10.5 Hz, 4-H).

5-*Ethyl*-6,7,8,9-*tetrahydrocyclohept*[b]*indol*-10(5H)-*one*.—(*a*) A solution of cycloheptindole (5.55 g), ethyl toluene-*p*-sulphonate (6.1 g), and sodium hydride (1.44 g), in anhydrous xylene (500 ml) was boiled under reflux (15 h). The cooled mixture was filtered, the filtrate evaporated under reduced pressure, and the crude product, m.p. 61—62 °C (6.2 g, 97%), recrystallized from absolute ethanol.

(*b*) A solution of DDQ (11.1 g) in tetrahydrofuran (100 ml) was added dropwise under nitrogen to a stirred, cooled (0 °C), solution of the 5-ethyl derivative (5.2 g) in aqueous THF (275 ml, 10% water). Stirring was continued for 2 h, then the solvent was evaporated under reduced pressure. The residue was chromatographed on alumina (300 g; IV) in ethyl acetate giving 5-*ethyl*-6,7,8,9-*tetrahydrocyclohept*[b]*indol*-10(5H)-*one* (4.49 g, 81%), m.p. 97—98 °C (from cyclohexane) (Found: C, 79.2; H, 7.5; N, 6.4. $C_{15}H_{17}NO$ requires C, 79.25; H, 7.55; N, 6.15%); δ 1.25 (3 H, t, CH_3CH_2), 1.6—2.1 (4 H, m), 2.6—3.0 (4 H, m), 3.95 (2 H, q, CH_2CH_3), 7.05—7.1 (3 H, m), and 8.35 (1 H, m, 4-H).

9,9-*Dibromo*-5-*ethyl*-6,7,8,9-*tetrahydrocyclohept*[b]*indol*-10(5H)-*one*.—The cycloheptindolone was brominated using PTAT; work-up in the usual way was followed by chromatography on alumina (IV), eluting with benzene–light petroleum (1:9). Recrystallization from chloroform–light petroleum gave the *dibromo derivative* (91%), m.p. 124—125 °C (Found: C, 47.05; H, 3.85; N, 4.0. $C_{15}H_{15}Br_2NO$ requires C, 46.75; H, 3.9; N, 3.65%); δ 1.3 (3 H, t), 1.8—2.35 (2 H, m), 2.85—3.2 (4 H, m), 4.05 (2 H, q), 7.1—7.8 (3 H, m), and 8.25 (1 H, m, 4-H).

5-*Ethylcyclohept*[b]*indol*-10(5H)-*one* (**70**).—The dibromo compound (3.3 g) was dehydrobrominated by lithium chloride (1.35 g) in boiling DMF (300 ml) (5 h). Work-up as described before gave, after recrystallization from chloroform–light petroleum (9:1), yellow crystals of the *cycloheptindolone* (**70**), m.p. 117—118 °C (Found: C, 80.9; H, 5.7; N, 6.15. $C_{15}H_{13}NO$ requires C, 80.7; H, 5.85; N, 6.25%); δ 1.35 (1 H, t), 4.6 (2 H, q) 6.62—7.34 (7 H, m), and 8.9 (1 H, m).

Acknowledgements

Our thanks are due to the University of Keele for a studentship (to M. G. H.), and to Professor K. Yamane for a gift of 3-phenylcyclohept[2,3-*b*]pyrrol-8-one.

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Received 6th February 1984; *Paper* 4/197