On the Reactions of (Vinylimino)phosphoranes and Related Compounds. Part 28.[1] Synthesis and Chemical Properties of Dicyclohepta[*b,d*]pyrrole Ring System

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A new synthesis of 6,7-dihydro-5*H*-dicyclohepta[*b,d*]pyrrole **10** consists of the reaction of cyclohepta-1,3,5-trienylimino(tributyl)phosphorane with tropone in an enamine alkylation process and subsequent condensation of the iminophosphorane moiety with a carbonyl function (aza-Wittig reaction). Hydride abstraction from **10** with Ph_3CBF_4 gives 5*H*-dicyclohepta[*b,d*]pyrrolium tetrafluoroborate **14**, which cannot be converted into 5*H*-dicyclohepta[*b,d*]pyrrole **15**. On the other hand, upon treatment with MnO_2, compound **10** is converted into 1*H*-dicyclohepta[*b,d*]pyrrole **16**, 3*H*-dicyclohepta[*b,d*]pyrrol-3-one **17** and 1*H*-dicyclohepta[*b,d*]pyrrol-1-one **18**. The chemical and spectral properties of **16**, **17** and **18**, together with their conversion into protonated or methylated compounds have been studied. Hydrogen abstraction from **16** with Ph_3CBF_4 gives the novel but unstable dicyclohepta[*b,d*]pyrrolium ion **4**. It is shown that compound **4** absorbs at shorter wavelength than the cycloheptazulenium ion **1**, its hydrocarbon analogue, because of the presence of an electronegative nitrogen atom; the spectrum exhibited fine structure, however, which resembled that of **1**.

It was suggested, on the basis of HMO calculations,[2] that the cyclohept[*a*]azulenium ion **1** would be a stable cation with 18π electrons. Compound **1** upon being successfully synthesized and characterized was found to have a fairly large pK_{R+} value (7.3) with its positive charge delocalized over the ring carbon atoms; the latter was established on the basis of spectral evidence.[3] Similarly, the related carbonyl compounds, 5*H*-,[4] 3*H*-,[5] and 1*H*-cyclohept[1,2-*a*]azulenones[6] have also been described. Furthermore, the oxygen analogues of the 7-5-7 ring system such as the dication **2**,[7] which is isoelectronic with **1**, and the cation **3**,[8] have also been prepared. Although 2-methoxy-3*H*-dicyclohepta[*b,d*]pyrrol-3-one has been prepared,[9] general synthetic methodology for the dicyclohepta[*b,d*]pyrrole ring system such as **4** has not hereto been explored (Fig. 1).

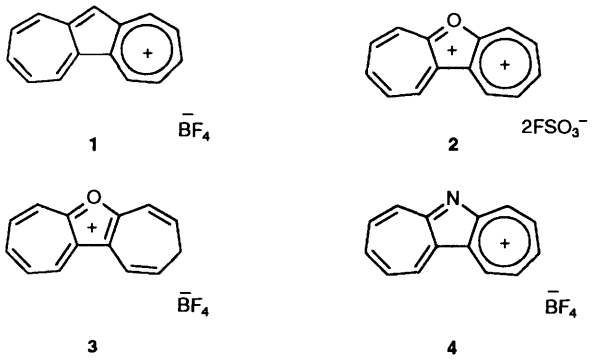


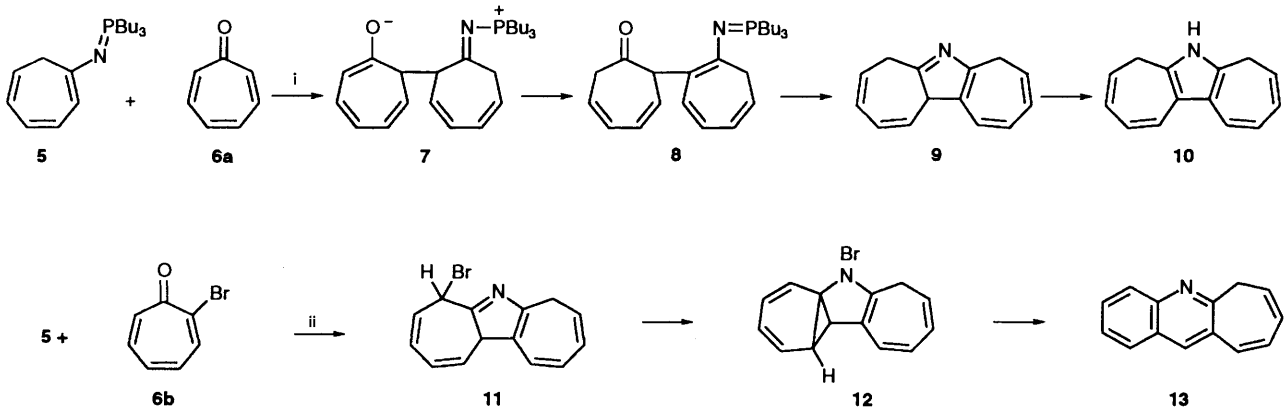
Fig. 1

Previously, we have demonstrated the utility of (vinylimino)-phosphoranes for the preparation of various kinds of heterocycles.[10] (Vinylimino)phosphoranes have been shown to react with tropone and its derivatives very easily to give the 1-azaazulene ring system.[11-13] On the basis of these studies, we have sought to synthesize the dicyclohepta[*b,d*]pyrrole ring system in a convenient fashion. Here we report such a synthesis together with the chemical properties of dicyclohepta[*b,d*]pyrrolium cation and its related compounds.

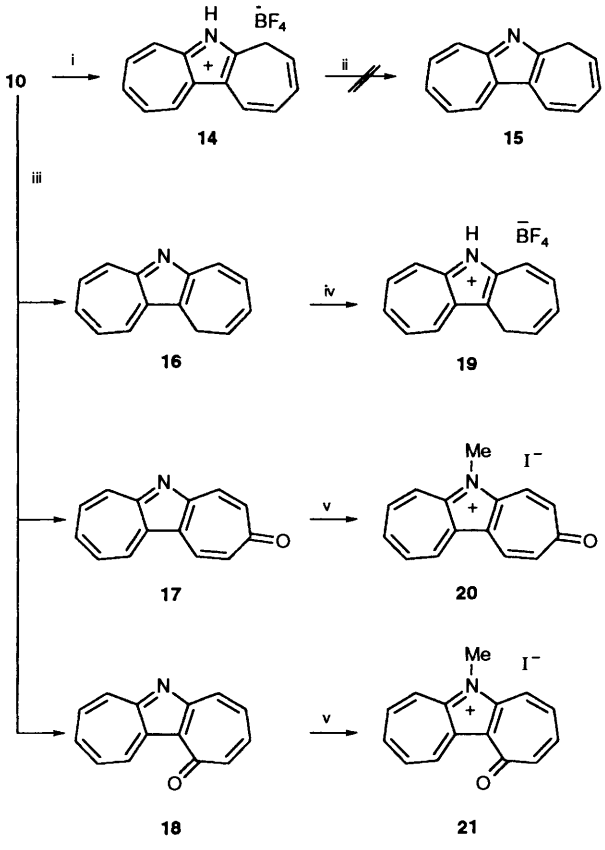
Results and Discussion

Our synthetic strategy for the dicyclohepta[*b,d*]pyrrole ring system involved the reaction of cyclohepta-1,3,5-trienylimino(tributyl)phosphorane **5**[14-16] with tropone **6a** or 2-bromotropone **6b**. The reaction of **5** with **6a** in benzene was carried out at room temperature for 24 h to give novel 6,7-dihydro-5*H*-dicyclohepta[*b,d*]pyrrole **10** in 34% yield. Compound **10** is unstable on silica gel and decomposed significantly. Thus, it was purified by column chromatography on Florisil. The postulated pathways for the formation of **10** are shown in Scheme 1.[11-13] Enamine-type alkylation of the iminophosphorane **5** onto C-2 of **6a** gives **7**. Hydrogen migration in **7** regenerates the (vinylimino)phosphorane moiety in **8**. The intermediate **8** then undergoes an intramolecular aza-Wittig reaction followed by hydrogen migration to give **10**. The structure of **10** was confirmed by high resolution mass spectrometry, elemental analysis of the salt **14** (*vide infra*), and ^1H NMR studies. Regarding the ^1H NMR spectrum, **10** has a symmetric structure and the chemical shifts and coupling patterns are in good agreement with the proposed structure.

On the other hand, the reaction of (vinylimino)phosphoranes with 2-halogenotropones has been shown to give the 1-azaazulene ring system in a single step.[11] Thus, the reaction of **5** with 2-bromotropone **6b**, carried out in benzene in the presence of triethylamine under reflux, gave 5*H*-cyclohepta[*b*]quinoline **13** as the product (Scheme 1). Enamine-type alkylation of **5** occurs onto C-7 of **6b**,[11] and the following hydrogen migration and aza-Wittig reaction would give **11**. Regarding the 1-azaazulene synthesis reported previously,[11-13] the intermediate **11** is expected to undergo dehydrobromination easily in the presence of NEt_3. However, **11** underwent rearrangement in the present reaction, possibly *via* **12**, to give **13**. The intermediate similar to **12** has been postulated previously in the rearrangement of a cycloheptapyrrole derivative to give a dihydroquinoline.[17] The structure of **13** was confirmed on the basis of the ^1H NMR and IR spectral data as well as the elemental analysis. Especially the evidence of 5*H*-isomer, not of 1*H*-isomer, was unequivocally manifested by the



Scheme 1 *Reagents and conditions:* i, room temp.; ii, reflux in benzene-NEt_3

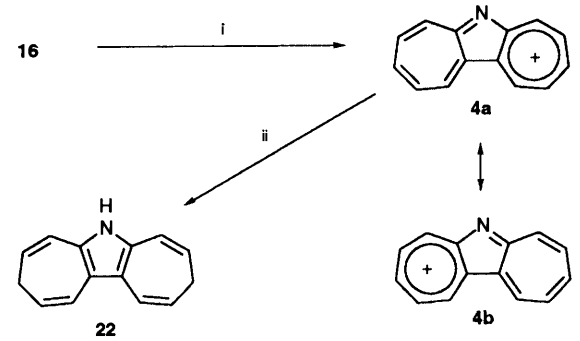


Scheme 2 *Reagents and conditions:* i, Ph_3CBF_4–CH_2Cl_2, room temp.; ii, NEt_3; iii, MnO_2–PhH, room temp.; iv, HBF_4–Ac_2O; v, MeI–CH_2Cl_2, room temp.

pseudo-contact ^1H NMR spectral data [relative downfield shifts (ppm/mol) of δ_H, Experimental] obtained by using $Eu(fod)_3$.

The hydride abstraction of **10** with Ph_3CBF_4 was completed at room temperature within 1.5 h to give, as a dark brown solid, 5*H*-dicyclohepta[*b*,*d*]pyrrolium tetrafluoroborate **14** (Scheme 2). The structure of **14** was supported by its elemental analysis and ^1H NMR, IR, and electronic spectral data (Table 1). Attempts to generate 5*H*-dicyclohepta[*b*,*d*]pyrrole **15** by treatment with triethylamine, however, caused significant decomposition, none of the expected product **15** being obtained. Previously, we have used NiO_2 and MnO_2 for the dehydrogenation of 1,8-dihydrocyclohepta[*b*]pyrrole to give 1-azaazulene.[11] Thus, upon treatment with MnO_2 at room temperature, compound **10** was converted into 1*H*-dicyclohepta[*b*,*d*]pyrrole **16**, 3*H*-dicyclohepta[*b*,*d*]pyrrol-3-one **17** and 1*H*-dicyclohepta[*b*,*d*]pyrrol-1-one **18** in 38, 19, and 2% yields, respectively (Scheme 2). On treatment with HBF_4 in acetic anhydride, **16** was converted into compound **19**. Unlike the case of **14**, both compounds **16** and **19** were stable, **16** being regenerated upon treatment of **19** with NEt_3. The structures of **16** and **19** were determined on the basis of elemental analyses and high resolution mass, ^1H NMR, IR, and electronic spectral data (Table 1). The methylene group located at C-1, not at C-5, for **16** was confirmed by the pseudo-contact ^1H NMR spectra obtained by using $Eu(fod)_3$ (Experimental section). Comparison of the ^1H NMR, IR, and mass spectra of **17** and **18** with those of 3*H*-cyclohept[1,2-*a*]azulen-3-one[5] and 1*H*-cyclohept[1,2-*a*]azulen-1-one,[4] respectively, and elemental analyses are in good agreement with the proposed structures. Compounds **17** and **18** reacted with MeI at room temperature to give 6-methyl-3-oxodicyclohepta[*b*,*d*]pyrrolium iodide **20** and 6-methyl-1-oxodicyclohepta[*b*,*d*]pyrrolium iodide **21**, respectively.

The hydride abstraction of **16** with Ph_3CBF_4 at room temperature afforded **4** in good yield. Compound **4** is very



Scheme 3 *Reagents and conditions:* i, Ph_3CBF_4–CH_2Cl_2, room temp.; ii, $NaBH_4$–CH_3CN, room temp.

unstable in air, decomposing significantly, and sparingly soluble in CD_3CN. Thus, no clear ^1H NMR spectrum and analytical data for **4** were obtained at this stage. However, the reduction of **4** with $NaBH_4$ afforded 6,9-dihydro-3*H*-dicyclohepta[*b*,*d*]pyrrole **22** in good yield, the structure of which was confirmed by high resolution mass and ^1H NMR spectral data. The reduction of **4** to give **22** is very similar to the reduction of **2** to give 6,8-dihydro-3*H*-dicyclohepta[*b*,*d*]furan.[7] In its electronic spectrum compound **4** (Table 1, Fig. 2) absorbs at a shorter wavelength than its hydrocarbon analogue **1** (Fig. 2).

Table 1 Electronic spectral data of dicycloheptapyrrole derivatives

Compound	Solvent	λ_{max}/nm (log ε)
4	MeCN	319 (4.49), 336 (4.53), 411 (3.46), 435 (3.83), 470 (3.17), 503 (2.99)
14	MeCN	261 (4.17), 294 (4.36), 374 (3.71), 478 (3.22)
16	EtOH	270 (4.54), 288 (4.51), 299 (4.51), 321 (4.42), 376 (4.04), 521 (3.39)
	EtOH–TFA	270 (4.51), 295 (4.43), 320 (4.34), 336 (4.26), 473 (3.81)
17	EtOH	279 (4.32), 324 (4.64), 337 (4.78), 378 (4.07), 398 (3.69), 551 (3.29)
	10% H_2SO_4	269 (4.27), 309, (4.59), 322 (4.76), 349 (4.04), 375 (3.56), 480 (3.61)
18	EtOH	267 (4.37), 320 (4.36), 332 (4.31), 398 (3.86), 480 (2.80)
	10% H_2SO_4	263 (4.50), 300 (4.23), 331 (3.99), 376 (3.63), 440 (3.59)
	conc. H_2SO_4	266 (4.07), 304 (4.54), 308 (4.58), 372 (3.72), 393 (3.75)
19	MeCN	268 (4.41), 333 (4.10), 472 (3.73)
20	MeCN	245 (4.51), 272 (4.37), 313 (4.71), 322 (4.78), 502 (3.61)
21	MeCN	260 (4.50), 312 (4.19), 322 (4.18), 337 (4.13), 388 (3.86), 462 (3.64)

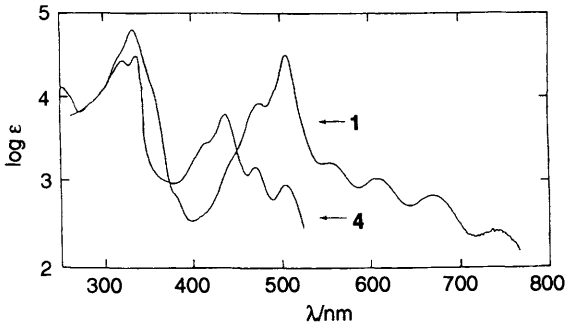
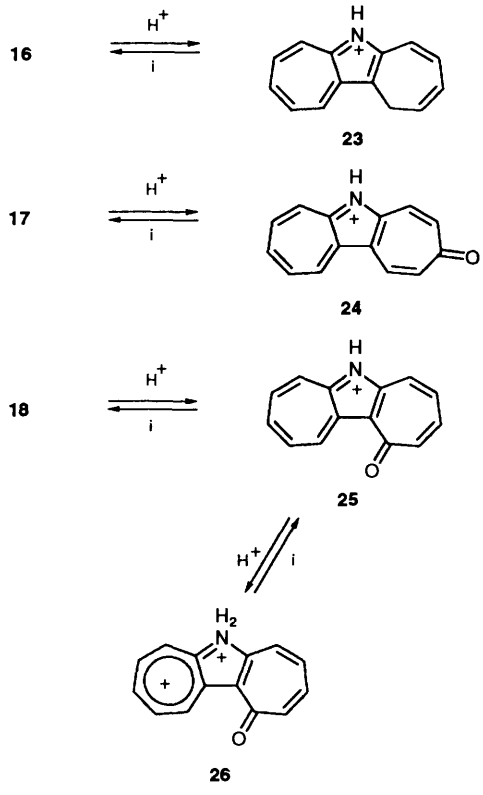


Fig. 2 Electronic spectra of compounds **1** and **4** in MeCN

Nevertheless, both compounds exhibit fine structure at longer wavelength and their spectra are closely similar to each other. In our previous studies of azuleno[1,2-*a*]azulene and its derivatives[18] as well as the 6-aza-analogue,[19] the strong electron-withdrawing properties of the nitrogen atom of the 1-azaazulene ring system, as compared to that of methoxycarbonyl group and even trifluoroacetyl group, are reflected by a remarkable bathochromic shift in the electronic spectra. Furthermore, it has been reported that 11-methoxycarbonylcyclohept[*a*]azulenium ion (pK_{R+}: 6.4) is less stable than that of the parent cation **1** (pK_{R+}: 7.3).[3] Thus, the instability of the dicyclohepta[*b*,*d*]pyrrolium ion **4** is attributable to the large electron-withdrawing property of the nitrogen atom.

The electronic spectral data for compounds **19**–**21** are also listed in Table 1. The spectrum of **16** in EtOH–TFA resembles that of **19** in MeCN, thus the protonation of **16** seems to occur on the nitrogen atom to give **23** in acidic media. The electronic spectrum of **17** also exhibited a bathochromic shift in 10% H_2SO_4 and resembled that of **20** in MeCN. Thus, the protonation of **17** occurs on the nitrogen atom to give **24**. Similarly, the protonation of **18** occurs in 10% H_2SO_4 to give **25**, the spectrum of which is similar to that of **21** in MeCN. Unlike compound **17**, the electronic absorption of compound **18** in conc. H_2SO_4 occurs at very short wavelengths; it is likely that this occurs because of further protonation on the nitrogen atom of **18** to give **26**. All the protonation processes to give **23**, **24**, **25** and **26** have been found to be reversible, compounds **16**, **17** and **18** being recovered upon addition of aqueous Na_2CO_3. Unlike the azulene analogues,[4–6] the formation of a 14π electronic system, such as that of **4**, was not observed in the protonations of **17** and **18**.

In conclusion, the utility of a (vinylimino)phosphorane for the preparation of a novel dicyclohepta[*b*,*d*]pyrrole ring system was demonstrated. It is clarified that dihydrocyclohepta-[*b*,*d*]pyrrolium ion is not stable as compared with its hydrocarbon analogue **1**, possibly because of the large electron-withdrawing property of the nitrogen atom.



Scheme 4 *Reagent:* i, aq. Na_2CO_3

Experimental

IR spectra were recorded on a Shimadzu IR-400 spectrometer. ^1H NMR spectra were recorded on a Hitachi R-90H spectrometer and the chemical shifts are given relative to internal $SiMe_4$ standard. *J* Values are given in Hz. High resolution mass spectra were run on a JEOL DX-300 spectrometer. Elemental analyses were performed at the Materials Characterization Central Laboratory of Waseda University. M.p.s were measured on a Büchi apparatus and are uncorrected. Cyclohepta[*a*]azulenium ion **1** was prepared according to the procedure reported in the literature.[4]

Preparation of 6,7-*Dihydro*-5H-*dicyclohepta*[b,d]*pyrrole* **10**.—A solution of cyclohepta-1,3,5-trienylimino(tributyl)phosphorane **5** (3.07 g, 10 mmol) and the tropone **6a** (1.17 g, 11 mmol) in benzene (20 cm^3) was stirred at room temp. for 22 h. The reaction mixture was then chromatographed on Florisil. The fractions eluted with benzene were concentrated, and the

residue was crystallized from hexane to give **10** (620 mg, 34%), m.p. 93 °C (decomp.) (from benzene–hexane); δ_H(90 MHz, $CDCl_3$) 3.10 (4 H, d, *J* 6.2, 5, 7-H), 5.38 (2 H, dt, *J* 10.8, 6.2, 4, 8-H), 6.00 (2 H, dd, *J* 10.8, 5.4, 3, 9-H), 6.12 (2 H, dd, *J* 10.6, 5.4), 6.63 (2 H, d, *J* 10.6) and 7.10–7.50 (1 H, br, NH); ν_{max}($CHCl_3$) 3448, 2998, 2941, 2820, 1567, 1465, 1419; *m/z* (rel. intensity) 195 (M^+, 65) and 194 (100) (Found: C, 86.5; H, 6.6; N, 7.0%; M^+, 195.1030. $C_{14}H_{13}N$ requires C, 86.11; H, 6.71; N, 7.17%; *M*, 195.1048).

Thermal Reaction of the Iminophosphorane **5** *with* 2-*Bromotropone* **6b**.—A solution of **5** (164 mg, 0.5 mmol), **6b** (93 mg, 0.5 mmol) and triethylamine (101 mg, 1 mmol) in benzene (2 cm^3) was heated under reflux for 21 h. The reaction mixture was purified through column chromatography on silica gel. The fractions eluted with $CHCl_3$ were further purified by TLC on silica gel (AcOEt–hexane, 1:3) to give the 5*H*-cycloheptaquinoline **13** as an oil; δ_H(90 MHz, $CDCl_3$) 3.55 (2 H, d, *J* 6.2, 5-H), 6.00 (1 H, dt, *J* 9.9, 6.2, 4-H), 6.16 (1 H, dd, *J* 9.9, 4.8, 3-H), 6.55 (1 H, dd, *J* 11.4, 4.8, 2-H), 7.06 (1 H, d, *J* 11.4, 1-H), 7.38–7.85 (3 H, m, 8, 9, 10-H), 8.03 (1 H, dd, *J* 7.5, 0.9, 7-H) and 8.05 (1 H, s, 11-H); relative downfield shifts (ppm mol^{-1}) of δ_H obtained by using Eu(fod)$_3$/CCl_4, 10.0 (7-H), 8.6 (5-H), 2.2 (4-H), 2.0 (1, 11-H), 1.7 (2, 3-H) and 1.0–2.0 (8, 9, 10-H); ν_{max}($CHCl_3$)/cm^{-1} 2942, 1622, 1591, 1488, 1420, 1147 and 917; ν_{max}(EtOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 227 (4.44), 2.54 (4.18, sh), 314 (3.97), 336 (3.74, sh); *m/z* (rel. intensity) 193 (M^+, 100) and 192 (22) (Found: C, 87.3; H, 5.4; N, 7.3%; M^+, 193.0893. $C_{14}H_{11}N$ requires C, 87.01; H, 5.74; N, 7.25%; *M*, 193.0892).

Hydride Abstraction of **10** *with Trityl Tetrafluoroborate*.—A solution of **10** (54 mg, 0.28 mmol) and Ph_3CBF_4 (92 mg, 0.28 mmol) in CH_2Cl_2 (1 cm^3) was stirred at room temp. for 1 h. The precipitate was filtered off and recrystallized from MeCN to give 5*H*-dicyclohepta[*b,d*]pyrrolium tetrafluoroborate **14** as a dark brown powder; m.p. 210–215 °C (decomp.) (from MeCN–AcOEt); δ_H(90 MHz, CD_3CN), 3.65 (2 H, d, *J* 6.0, 5-H), 5.61 (1 H, dt, *J* 9.7, 6.0, 4-H), 6.20 (1 H, dd, *J* 9.7, 6.0, 3-H), 6.60 (1 H, dd, *J* 11.7, 6.0, 2-H), 7.20 (1 H, d, *J* 11.7, 1-H), 8.10–9.10 (5 H, m, 7, 8, 9, 10, 11-H) and 11.70–12.30 (1 H, br, NH); ν_{max}(KBr)/cm^{-1} 1583, 1512, 1467, 1436, 1331, 1293, 1081, 1064 and 1038 (Found: C, 59.9; H, 4.1; N, 4.9. $C_{14}H_{12}NBF_4$ requires C, 59.83; H, 4.30; N, 4.98%).

Oxidation of **10** *with* MnO_2.—A suspension of **25** (390 mg, 2 mmol) and MnO_2 (1.74 g, 20 mmol) in benzene (100 cm^3) was stirred for 1 h at room temp. The reaction mixture was filtered through Celite and the filtrate was concentrated. The resulting residue was subjected to TLC on silica gel (AcOEt–EtOH, 5:1) to give 1*H*-dicyclohepta[*b,d*]pyrrole **16** (147 mg, 38%), 3*H*-dicyclohepta[*b,d*]pyrrole-3-one **17** (39 mg, 9%) and 1*H*-dicyclohepta[*b,d*]pyrrol-1-one **18** (7 mg, 2%).

For **16**: oil; δ_H(90 MHz, $CDCl_3$) 3.56 (2 H, d, *J* 5.7, 1-H), 5.82 (1 H, dt, *J* 10.6, 5.7, 2-H), 6.07 (1 H, dd, *J* 10.6, 5.9, 3-H), 6.60 (1 H, dd, *J* 11.4, 5.9, 4-H), 7.28 (1 H, d, *J* 11.9, 5-H), 7.40–7.70 (3 H, m, 8, 9, 10-H), 8.20–8.35 (1 H, m, 11-H) and 8.35–8.52 (1 H, m, 7-H); relative downfield shifts (ppm mol^{-1}) of δ_H obtained by using Eu(fod)$_3$/CCl_4, 8.4 (5-H), 7.5 (7-H), 2.1 (1-H), 1.9 (11-H), 1.3 (4-H) and 1.2 (2, 3-H), 1.0 (8, 9, 10-H); ν_{max}($CHCl_3$)/cm^{-1} 2943, 1633, 1598, 1481, 1457, 1436, 1410 and 1378; *m/z* (rel. intensity) 193 (M^+, 75) and 192 (100) (Found: M^+, 193.0893. $C_{14}H_{11}N$ requires *M*, 193.0892).

For **17**: violet needles; m.p. 195 °C (decomp.) (from EtOH); δ_H(90 MHz; $CDCl_3$) 6.94 (1 H, dd, *J* 12.1, 2.4, 2-H), 7.24 (1 H, dd, *J* 12.3, 2.4, 4-H), 7.85–8.15 (5 H, m, 1, 5, 8, 9, 10-H) and 8.75–8.97 (2 H, m, 7, 11-H); ν_{max}($CHCl_3$)/cm^{-1} 2994, 1605, 1587, 1495, 1410, 1357 and 1330; *m/z* (rel. intensity) 207 (M^+, 24) and 179 (M – CO, 100) (Found: C, 81.25; H, 4.2; N, 6.7%; M^+, 207.0687. $C_{14}H_9NO$ requires C, 81.14; H, 4.38; N, 6.76%; *M*, 207.0685).

For **18**: orange needles; m.p. 120 °C (decomp.) (from benzene–hexane); δ_H(90 MHz; $CDCl_3$) 7.10–7.27 (3 H, m, 2, 3, 4-H), 7.90–8.20 (4 H, m, 5, 8, 9, 10-H), 8.75–8.95 (1 H, m, 7-H) and 10.50–10.65 (1 H, m, 11-H); ν_{max}($CHCl_3$)/cm^{-1} 3002, 2967, 1598, 1576, 1569, 1480, 1457, 1418, 1390, 1335, 1297, 1274, 1071 and 817; *m/z* (rel. intensity) 207 (M^+, 14) and 179 (M – CO, 100) (Found: C, 81.3; H, 4.2; N, 6.8%; M^+, 207.0692. $C_{14}H_9NO$ requires C, 81.14; H, 4.38; N, 6.76%; *M*, 207.0685.

Preparation of 1H-*Cyclohepta*[b,d]*pyrrolium Tetrafluoroborate* **19**.—To a stirred solution of **16** (35 mg, 0.18 mmol) in acetic anhydride (2 cm^3) was added 42% aqueous fluoroboric acid (200 mg, 1 mmol) dropwise, and the mixture was stirred for 30 min at room temp. To this mixutre was added ether (20 cm^3), and the mixture was stirred for a further 2.5 h. The precipitate was filtered off to give **14**: dark brown powder; m.p. 185 °C (decomp.) (from MeCN–AcOEt); δ_H(90 MHz; CD_3CN) 3.59 (2 H, d, *J* 5.6, 1-H), 5.97 (1 H, dd, *J* 10.2, 5.6, 2-H), 6.23 (1 H, ddd, *J* 10.2, 4.2, 2.3, 3-H), 6.99 (1 H, d, *J* 4.2, 2-H), 7.02 (1 H, d, *J* 2.3, 5-H), 8.16–8.45 (3 H, m, 8, 9, 10-H), 8.60–8.82 (1 H, m, 11-H), 8.82–9.10 (1 H, m, 7-H) and 11.70–12.20 (1 H, br, NH); ν_{max}(KBr)/cm^{-1} 1629, 1591, 1559, 1506, 1470, 1443, 1373, 1327, 1290, 1054 and 1036 (Found: C, 59.7; H, 4.65; N, 5.1. $C_{14}H_{12}NBF_4$ requires C, 59.83; H, 4.30; N, 4.98%).

Preparation of 6-*Methyl*-3-*oxodicyclohepta*[b,d]*pyrrolium Iodide* **20**.—A solution of **17** (41.4 mg, 0.2 mmol) and MeI (1 cm^3) in dichloromethane (1 cm^3) was stirred at room temp. for 5 days. The precipitate was filtered off to give **20** as dark violet prisms; m.p. above 300 °C (from MeCN–AcOEt) (Found: C, 51.5; H, 3.7; N, 4.5. $C_{15}H_{12}INO$ requires C, 51.60; H, 3.46; N, 4.01%.

Preparation of 6-*Methyl*-1-*oxodicyclohepta*[b,d]*pyrrolium Iodide* **21**.—A solution of **18** (6 mg, 0.29 mmol) and MeI (1 cm^3) in CH_2Cl_2 (1 cm^3) was stirred at room temp. for 24 h. The reaction mixture was concentrated and the precipitate filtered off to give **21** as dark violet prisms; m.p. above 300 °C (from MeCN–AcOEt) (Found: C, 51.4; H, 3.7; N, 4.35. $C_{15}H_{12}INO$ requires C, 51.60; H, 3.46; N, 4.01%).

Preparation of Dicyclohepta[b,d]*pyrrolium Tetrafluoroborate* **4**.—A solution of **16** (79 mg, 0.41 mmol) and trityl tetrafluoroborate (243 mg, 0.8 mmol) in CH_2Cl_2 (5 cm^3) was stirred for 24 h at room temp. The precipitate was filtered under nitrogen atmosphere to give **4** as greyish green plates; m.p. 160 °C (decomp.); ν_{max}(KBr)/cm^{-1} 2977, 1598, 1441, 1416, 1307, 1201, 1067, 1032 and 767.

Reduction of the Cation **4**.—A solution of **4** (22 mg, 0.08 mmol) and $NaBH_4$ (3 mg, 0.08 mmol) in MeCN (1 cm^3) was stirred for 10 min at room temp. The reaction mixture was then extracted with benzene, and the extract dried (Na_2SO_4) and evaporated to give **22**; δ_H(90 MHz; $CDCl_3$) 3.09 (4 H, t, *J* 5.4, 3, 9-H), 5.12–5.60 (2 H, m, 2, 10-H), 5.80–6.20 (4 H, m, 4, 5, 7, 8-H), 6.30–6.70 (2 H, m, 1, 11-H) and 7.50–7.80 (1 H, br, NH); ν_{max}($CHCl_3$)/cm^{-1} 3446, 3003 and 1556; *m/z* (rel. intensity) 195 (M^+, 100) (Found: M^+, 195.1034. $C_{14}H_{13}N$ requires *M*, 195.1049).

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