Ferrocene Derivatives. Part 24.[1] Synthesis of Dihydro-2-pyrindines and Dihydro-3*H*-2-cyclopent[*c*]azepines by Photolysis of their Cyclopentadienyliron Derivatives

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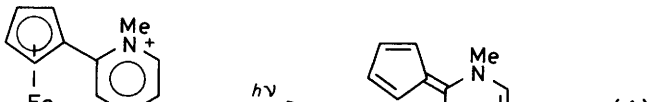
Bischler-Napieralski type cyclizations of *N*-acyl-2-ferrocenylethylamine and *N*-acyl-3-ferrocenylpropylamine lead respectively to cyclopentadienyl(dihydro-2-pyrindin-5-yl)iron and cyclopentadienyl(tetrahydrocyclopent[*c*]azepine)iron derivatives. Photolysis of their quarternary ammonium salts liberates the metal-free azabicyclic systems.

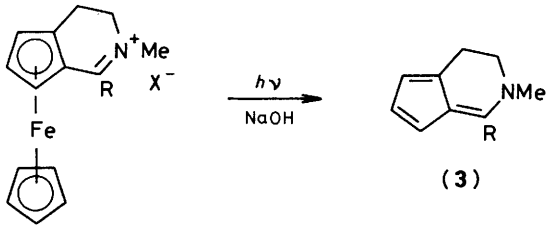
It has long been known that despite their remarkable thermal stability, α-ferrocenyl carbocations are distinctly light sensitive, undergoing cleavage to fulvenes.[2] Nesmeyanov and his co-workers[3] further established that similar photolytic cleavage occurs with ferrocenes bearing a partial positive charge at an α-position. The photolysis of the pyridinium salt (**1**) and the analogous cleavage of ferrocenylquinolinium salts represent typical examples of their results.



(1)

(**1**)

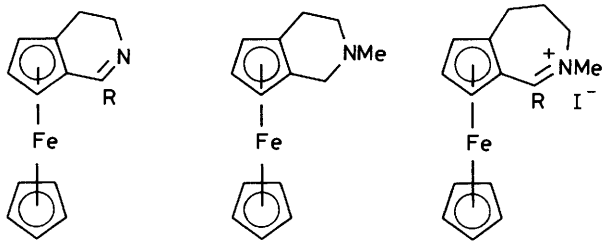
With a view to extending this reaction to the formation of fused bi- and poly-cyclic systems, one of us (I. U. K.) first effected the photolysis of the known[4] pyrindinyliron complex (**2a**; X = I) to the dihydropyrindine derivative (**3a**) in 1979. The work was interrupted by his death, then briefly continued by the author of reference 5, and is now being extended. The publication without acknowledgement,[5] of the formation of a very impure sample of compound (**3a**) prompts us to record our results to date.



(2) (3)

a ; R = Me
b ; R = Ph
c ; R = H

The quaternary salt (**2a**) is readily formed[4] from the imine (**4a**), itself obtained by Bischler-Napieralski type cyclisation of *N*-acetyl-2-ferrocenylethylamine. The analogous *N*-benzoyl derivative cyclises similarly to the dihydropyridoferrocene (**4b**), which reacts smoothly with iodomethane to afford the quaternary salt (**2b**; X = I). However, in conformity with earlier experiments,[4] the parent heterocycle (**4c**) failed to quaternise under these conditions. Moreover, although on treatment with dimethyl sulphate, solutions of this orange imine (**4c**) acquired the characteristic purple colour of the salts (**2**), we were unable to isolate the expected product even as the tetrafluoroborate salt. This salt was therefore prepared by an alternative route, the dehydrogenation of the known[4] *N*-methyltetrahydropyridoferrocene (**5**) with triphenylmethyl tetrafluoroborate.

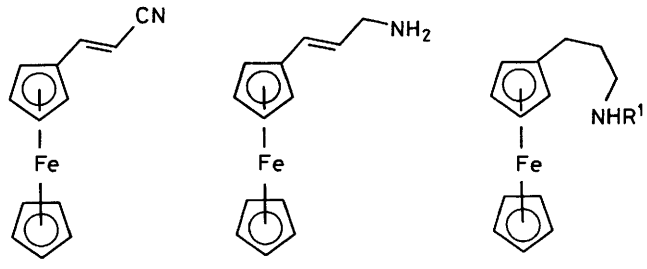


(4) (5) (6)

This reaction occurs rapidly at 0 °C and in excellent yield (86%). By contrast, we have been unable to dehydrogenate the dihydropyridoferrocenes (**4**) or further dehydrogenate the salts (**2**) with the same or several other reagents.

Each of the salts (**2a**—**c**) suffers smooth photodecomposition under the aqueous alkaline conditions which the Soviet workers[3] had found suitable for reaction (1).

In order to extend this photochemical route we then prepared the seven-membered ring analogues (**6a**,**b**). To obtain these, 3-ferrocenylacrylonitrile (**7**), readily available[6] by condensation of ferrocenecarbaldehyde with acetonitrile, was reduced first to the primary unsaturated amine (**8**) and then by catalytic hydrogenation to 3-ferrocenylpropanamine (**9a**). Its *N*-acetyl

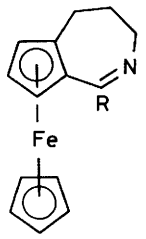


(7) (8) (9)

a; R^1 = H
b; R^1 = Ac
c; R^1 = Bz

(**9b**) and *N*-benzoyl derivative (**9c**) were prepared using acetic anhydride and benzoyl chloride respectively. The former was cyclised by phosphorus oxychloride under the conditions previously employed to give the 6-membered ring imines (**4**), but cyclisation of the benzamide (**9c**) was more successfully achieved with 'polyphosphate ester' following the method of Kanaoka *et al.*[7]

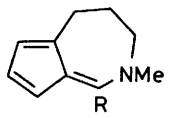
The corresponding quaternary salts (**6a**,**b**) again underwent smooth photolysis to yield the expected iron-free heterocycles (**11a**,**b**). All these fulvenoid tertiary amines (**3**) and (**11**) are



(**10**)

a ; R = Me

b ; R = Ph



(**11**)

relatively unstable both thermally and oxidatively, but all could be obtained in crystalline, essentially analytically pure form and characterised further by their n.m.r. spectra.

Experimental

All reactions were conducted under nitrogen. Alumina for chromatography had been neutralised with ethyl acetate and dried at 150 °C. 2-Ferrocenylethylamine, the salt (**2a**), the imine (**4c**), and the amine (**5**) were prepared as previously described.[4] 3-Ferrocenylacrylonitrile (**7**) was obtained by an improved procedure for the condensation of ferrocenecarbaldehyde with acetonitrile[8] without isolation of the intermediate carbinol.

N-*Benzoyl-2-ferrocenylethylamine*.—Benzoyl chloride (5.11 g, 36 mmol) and ferrocenylethylamine (4.19 g, 18 mmol) were warmed to 80 °C in toluene (20 cm^3) for 0.5 h. The mixture was then poured into cold water and the toluene layer separated, dried (Na_2SO_4), and evaporated. The residue was chromatographed on alumina, the product being eluted with ether. Recrystallisation from toluene–light petroleum (b.p. 40—60 °C) gave the yellow amide (3.96 g, 65%) as plates, m.p. 109 °C; $\nu_{max.}$(KCl) 3 395 and 1 640 cm^{-1}; $\delta(CDCl_3)$ 2.64 (2 H, t, CH_2C_5), 3.55 (2 H, q, CH_2N), 4.15 (9 H, m, C_5H_5, C_5H_4), 6.35 (1 H, s, NH), 7.40 (3 H, m), and 7.71 (2 H, m, C_6H_5) (Found: C, 68.5; H, 5.6; N, 4.2. $C_{19}H_{19}FeNO$ requires C, 68.5; H, 5.7; N, 4.2%).

2-*Cyanovinylferrocene* (3-*Ferrocenylacrylonitrile*) (**7**).—Our improved method (*cf.* ref. 8) follows a procedure for the synthesis of cinnamonitrile.[9]

To potassium hydroxide pellets (0.26 g, 4.7 mmol) heated under reflux in acetonitrile (12 cm^3) with magnetic stirring, a solution of ferrocenecarbaldehyde (1.0 g, 4.7 mmol) in acetonitrile (3 cm^3) was added and heating continued for 20 min. After cooling, the mixture was filtered and excess of acetonitrile removed under reduced pressure. The residual oil, which crystallised with time, was chromatographed on alumina using toluene as solvent. The main orange-red band was evaporated and the orange residue crystallised from light petroleum (b.p. 30—40 °C) to give the product as a mixture of *E* and *Z* isomers (800 mg, 73%), m.p. 70 °C, suitable for the following step; $\nu_{max.}$(KCl) 2 210, 1 620, 1 105, 1 000, and 820 cm^{-1} (Found: C, 65.7; H, 4.6; N, 5.7. Calc. for $C_{13}H_{11}FeN$: C, 65.9; H, 4.7; N, 5.9%).

3-*Amino*-1-*ferrocenylpropene* (**8**).—The cyano compound (**7**) (7.2 g, 30 mmol) in dry diethyl ether (70 cm^3) was added dropwise to a solution of lithium aluminium hydride (2.8 g, 75 mmol) in the same solvent (20 cm^3) and the mixture stirred at room temperature overnight. Excess hydride was destroyed by the addition of moist ether followed by water. The mixture was then filtered, the organic layer separated, dried ($MgSO_4$) and evaporated and the residual amine (6.1 g, 83%) distilled, b.p. 111 °C/0.3 Torr; $\nu_{max.}$(film) 3 385, 3 100, and 1 615 cm^{-1}; $\delta(CDCl_3)$ 1.45 (2 H, br s, NH_2), 3.33 (2 H, br d, CH_2), 4.20 (5 H, s, C_5H_5), 4.20 (2 H, m), and 4.32 (2 H, m, C_5H_4), and 6.10 (2 H, m, CH=) (Found: C, 64.5; H, 6.4; N, 5.8. $C_{13}H_{15}FeN$ requires C, 64.75; H, 6.3; N, 5.8%).

3-*Ferrocenylpropylamine* (**9a**).—The unsaturated amine (**8**) (0.63 g, 2.6 mmol) in ethanol (10 cm^3) containing 3 equivalents of concentrated hydrochloric acid and 10% palladium on charcoal (0.1 g) was shaken in a hydrogen atmosphere until gas uptake ceased (*ca.* 1 h). The solution was filtered and evaporated and the residue taken up in ether. This solution was washed with 2M aqueous sodium hydroxide, dried ($MgSO_4$), and evaporated. Distillation of the residue at 195 °C (bath temp.)/0.1 Torr gave 3-ferrocenylpropylamine (**9a**) (0.6 g, 95%) as an orange oil; $\nu_{max.}$(film) 3 385, 3 100, 1 100, and 1 000 cm^{-1}; $\delta(CDCl_3)$ 1.65 (4 H, m, $CH_2CH_2NH_2$ and NH_2), 2.38 (2 H, m, C_5CH_2), 2.72 (2 H, t, CH_2N), 4.08 (9 H, m, C_5H_5 and C_5H_4) (Found: C, 63.0; H, 6.7; N, 5.9. $C_{13}H_{17}FeN$ requires C, 64.2; H, 7.0; N, 5.8%). The poor analysis is attributed to absorption of carbon dioxide.

Its *N*-acetyl derivative (**9b**) (3.18 g, 68%) was obtained by heating the amine (**9a**) (4.0 g, 16 mmol) and acetic anhydride (3.1 cm^3) in dry toluene (30 cm^3) at 80 °C for 30 min and isolated by alumina chromatography, eluting with ether: yellow plates (from cyclohexane), m.p. 73—74 °C; $\nu_{max.}$(KCl) 3 225 and 1 635 cm^{-1} (Found: C, 63.1; H, 6.7; N, 4.8. $C_{15}H_{19}FeNO$ requires C, 63.2; H, 6.7; N, 4.9%).

The *N*-benzoyl derivative (**9c**) (3.15 g, 68%) was obtained similarly from the amine (**9a**) (3.21 g, 13.2 mmol) and benzoyl chloride (3.71 g, 26.4 mmol) as yellow plates (from toluene), m.p. 87—88 °C; $\nu_{max.}$(KCl) 3 340 and 1 645 cm^{-1}; $\delta(CDCl_3)$ 1.84 (2 H, m, CH_2CH_2N), 2.46 (2 H, t, C_5CH_2), 3.47 (2 H, q, CH_2N), 4.08 (9 H, m, C_5H_5 and C_5H_4), 6.23 (1 H, s, NH), 7.44 (3 H, m), and 7.69 (2 H, m, C_6H_5) (Found: C, 69.0; H, 6.0; N, 3.9. $C_{20}H_{21}FeNO$ requires C, 69.2; H, 6.1; N, 4.0%).

η-*Cyclopentadienyl*[(4a,5,6,7,7a-η)-3,4-*dihydro*-1-*phenyl*-2-*pyrindin*-5-*yl*]*iron* (**4b**) *and Its Methiodide* (**2b**; X = I).—Phosphorus oxychloride (5.1 cm^3) was added to a well-stirred solution of *N*-benzoyl-2-ferrocenylethylamine (1.0 g, 3 mmol) in toluene (16 cm^3) and the mixture warmed to 80 °C for 1 h, then allowed to cool and added to ice–water. After separating the toluene layer, the purple aqueous layer was made alkaline with 2M aqueous potassium hydroxide causing a colour change to yellow, and extracted with toluene. This extract was concentrated and chromatographed on alumina, eluting with ether. The major fraction when evaporated left a brownish-yellow oil (850 mg, 90%) which solidified on refrigeration and was recrystallised from ether–light petroleum (b.p. 40—60 °C), m.p. 87 °C; $\nu_{max.}$(KCl) 2 920, 1 600, and 1 420 cm^{-1}; $\delta(CDCl_3)$ 2.3 (2 H, br m, CH_2CH_2N), 3.8 (2 H, br m, CH_2N), 4.15 (5 H, s, C_5H_5), 4.35 (3 H, m, C_5H_3), 7.39 (3 H, m), and 7.65 (2 H, m, C_6H_5) (Found: C, 72.3; H, 5.6; N, 4.4. $C_{19}H_{17}FeN$ requires C, 72.4; H, 5.4; N, 4.45%).

This imine (1 g, 3.2 mmol) in toluene (5 cm^3) was treated with an excess of iodomethane overnight. The precipitated methiodide (**2b**; X = I) was then filtered off and reprecipitated from ethanol solution with diethyl ether as a purple solid (0.72 g, 50%), m.p. 107 °C; $\nu_{max.}$(KCl) 3 360, 1 600, 1 450, 1 405, and 800 cm^{-1}; δ($CDCl_3$) 3.05 (2 H, m, 4-H), 3.67 (3 H, s, CH_3), 4.30 (2 H, m, 3-H), 4.61 (5 H, s, C_5H_5), 4.95 (3 H, 'd', 5-, 6-, and 7-H), and 7.60 (5 H, m, C_6H_5) (Found: C, 52.1; H, 4.3; N, 3.0. $C_{20}H_{20}FeIN$ requires C, 52.5; H, 4.4; N, 3.1%).

η-*Cyclopentadienyl*[(5a,6,7,8,8a-η)-3,4,5,6-*tetrahydro*-1-*methylcyclopent*[c]*azepin*-6-*yl*]*iron* (**10a**) *and Its Methiodide* (**6a**).—The procedure of the preceding experiment was repeated using *N*-acetyl-3-ferrocenylpropylamine (**9b**) (1.5 g, 5 mmol) and phosphorus oxychloride (7.1 cm^3) in toluene (10 cm^3). The product (**6a**) (1.1 g, 78%) was isolated by distillation at 90 °C (bath temp.)/0.001 Torr as a yellow-brown oil; $\nu_{max.}$(film) 1 625, 1 260, and 1 000 cm^{-1} (Found: C, 67.0; H, 6.3; N, 5.3. $C_{15}H_{17}FeN$ requires C, 67.4; H, 6.4; N, 5.25%). Treatment of this imine (1.0 g, 3.7 mmol) in toluene (15 cm^3) with an excess of iodomethane gave the methiodide (**6a**) (1.2 g, 78%) as purple crystals (from ethanol), m.p. 222 °C; $\nu_{max.}$(KCl) 1 610, 1 410, and 1 000 cm^{-1} (Found: C, 46.6; H, 4.8; N, 3.3. $C_{16}H_{20}FeIN$ requires C, 47.0; H, 4.9; N, 3.4%).

η-*Cyclopentadienyl*[(5a,6,7,8,8a-η)-3,4,5,6-*tetrahydro*-1-*phenylcyclopent*[c]*azepin*-6-*yl*]*iron* (**10b**) *and Its Methiodide* (**6b**).—*N*-Benzoyl-3-ferrocenylpropylamine (**9c**) (1 g, 2.8 mmol) in toluene (5 cm^3) was added to 'polyphosphate ester'[7] (**6g**) in toluene (20 cm^3) and the mixture refluxed for 4 h; it was then cooled and poured into 5% hydrochloric acid. The aqueous layer was separated, made alkaline with 2M aqueous sodium hydroxide and extracted with toluene. The dried toluene solution was evaporated and the residual brown oil chromatographed on alumina using ether as eluant. The main fraction yielded the imine (**10b**) (0.40 g, 42%); $\nu_{max.}$(film) 3 100, 2 930, 2 850, and 1 620 cm^{-1} (Found: C, 73.2; H, 5.9; N, 4.0. $C_{20}H_{19}FeN$ requires C, 73.0; H, 5.8; N, 4.25%). When this imine (**10b**) (0.3 g, 0.9 mmol) was left with excess of iodomethane in toluene (5 cm^3) overnight, the methiodide (**6b**) (0.35 g, 81%) was precipitated; it formed purple crystals from ethanol, m.p. 186—187 °C; $\nu_{max.}$(KCl) 3 050, 1 605, 1 400, and 1 370 cm^{-1}; δ($CDCl_3$) *ca.* 2.5 (2 H, br m, 4-H), 2.9 (2 H, br m, 5-H), 3.50 (3 H, s, CH_3), 4.22 (2 H, m, 3-H), 4.51 (5 H, s, C_5H_5), 3.87, 4.82, and 5.13 (each 1 H, m, 6-, 7-, and 8-H), and 7.59 (5 H, br s, C_6H_5) (Found: C, 53.5; H, 4.6; N, 2.9. $C_{21}H_{22}FeIN$ requires C, 53.5; H, 4.7; N, 3.0%).

η-*Cyclopentadienyl*-[(4a,5,6,7,7a-η)-3,4-*dihydro*-2-*methyl*-4a*H*-2-*pyrindin*-4a-*yl*]*iron Tetrafluoroborate* (**2c**; X = BF_4).—Triphenylmethyl tetrafluoroborate (0.65 g, 1.9 mmol) in dichloromethane (8 cm^3) was added to a solution of η-cyclopentadienyl[(4a,5,6,7,7a-η)-1,2,3,4-tetrahydro-2-methyl-4a*H*-2-pyrindin-4a-yl]iron[3] (**5**) (0.5 g, 1.9 mmol) in the same solvent (5 cm^3) at 0 °C and the mixture stirred at this temperature for 15 min. After removal of solvent, crystallisation of the residue from ethanol allowed separation of the pure salt (**2c**; X = BF_4) (0.56 g, 84%) as purple crystals, m.p. 137—138 °C; $\nu_{max.}$(KCl) 3 100, 1 640, 1 490, 1 330, and 710 cm^{-1}; δ[$(CD_3)_2CO$] 2.06 (2 H, m, 4-H), 3.66 (3 H, s, CH_3), 3.99 (2 H, br m, 3-H), 4.58 (5 H, s, C_5H_5), 4.93 (1 H, m), and 5.04 (2 H, m, 5-, 6-, and 7-H), and 9.22 (1 H, br s, 1-H) (Found: C, 49.4; H, 4.8; N, 4.0. $C_{14}H_{16}BF_4FeN$ requires C, 49.3; H, 4.7; N, 4.1%).

Photolyses: General procedure.—Each of the methiodides was dissolved in water, sodium hydroxide was added and the solution was then irradiated through a quartz tube with a medium-pressure mercury lamp in the centre of an annular (Hanovia) apparatus until the initial, deep red-purple colour had changed to orange-yellow or brown (6—15 h). The solutions were then filtered to remove insoluble iron compounds and extracted with ether. The ether extracts were, in turn, extracted with 10% aqueous sulphuric acid and the basic products recovered from the acid extracts by addition of 10% aqueous sodium hydroxide and re-extraction into toluene. Finally the dried toluene solutions were evaporated.

3,4-*Dihydro*-1,2-*dimethyl*-2H-2-*pyrindine* (**3a**) (300 mg, 81%) was obtained in this way from the methiodide (**2a**; X = I)[3] (1 g, 2.5 mmol) in water (5 cm^3) and 10% aqueous sodium hydroxide (20 cm^3). It formed very pale yellow crystals, m.p. 75 °C (from cyclohexane); $\nu_{max.}$(KCl) 1 510, 1 480, 1 420, and 930 cm^{-1}; δ($CDCl_3$) 2.23 (3 H, s, C-CH_3), 2.79 (2 H, dt, 4-H), 3.07 (3 H, s, N-CH_3), 3.38 (2 H, t, $J_{3,4}$ 7.5 Hz, 3-H), 5.88 (1 H, m, 5-H), 6.16 (1 H, dd, $J_{6,7}$ *ca.* 4.5 Hz, 6-H?), and 6.28 (1 H, dd, 7-H?); M^+, 147.1044 ($C_{10}H_{13}N$ calcd.: 147.1048) and major fragment ions at *m/z* 146.0965 (base peak; $C_{10}H_{12}N$: 146.0970) 131.0731 (C_9H_9N: 131.0735), and 103.0555 (C_8H_7: 103.0548) (Found: C, 81.8; H, 8.9; N, 9.5. $C_{10}H_{13}N$ requires C, 81.6; H, 8.9; N, 9.5%).

3,4-*Dihydro*-2-*methyl*-1-*phenyl*-2H-2-*pyrindine* (**3b**) (0.55 g, 30%) was obtained from the methiodide (**2b**; X = I) (4.0 g, 8.75 mmol) in water (50 cm^3) plus 10% aqueous sodium hydroxide (70 cm^3) as a pale yellow solid, m.p. 94 °C (from light petroleum); $\nu_{max.}$(KCl) 2 925, 1 600, 1 350, and 800 cm^{-1}; δ($CDCl_3$) 2.98 (5 H, s + t, CH_3 + 4-H), 3.63 (2 H, t, *J* 7 Hz, 3-H), 5.79 (1 H, dd), 6.02 (1 H, m), and 6.02 (1 H, dd, 5-, 6-, and 7-H), and 7.41 (5 H, m, C_6H_5) (Found: C, 85.6; H, 7.3; N, 6.7. $C_{15}H_{15}N$ requires C, 86.1; H, 7.2; N, 6.7%).

3,4-*Dihydro*-2-*methyl*-2H-2-*pyrindine* (**3c**) (0.21 g, 36%) was obtained from the tetrafluoroborate salt (**2c**; X = BF_4) (1.5 g, 4.5 mmol) in water (30 cm^3) and 10% aqueous sodium hydroxide (60 cm^3). It was purified by chromatography on alumina, eluting with ether, and crystallised from light petroleum (b.p. 30—40 °C) forming yellow crystals, m.p. 45 °C; $\nu_{max.}$(KCl) 3 080, 2 920, 1 610, and 1 100 cm^{-1}; δ($CDCl_3$) 2.88 (2 H, dt, 4-H), 3.10 (3 H, s, CH_3), 3.33 (2 H, t, 3-H), 5.96 (1 H, m, 5-H), 6.24 (2 H, m, 6- and 7-H), and 7.10 (1 H, d, 1-H) (Found: C, 80.6; H, 8.1; N, 10.4. $C_9H_{10}N$ requires C, 81.15; H, 8.3; N, 10.5%).

2,3,4,5-*Tetrahydro*-1,2-*dimethylcyclopent*[c]*azepine* (**11a**) (600 mg, 76%) was obtained from the methiodide (**6a**) (2 g, 5 mmol) in water (20 cm^3) and 10% aqueous sodium hydroxide (80 cm^3) after purification by chromatography on alumina. Elution with ether and recrystallisation from cyclohexane gave almost colourless crystals, m.p. 65 °C; $\nu_{max.}$(KCl) 1 510, 1 480, 1 420, and 930 cm^{-1}; δ($CDCl_3$) 2.08 (2 H, m, 4-H), 2.39 (3 H, s, C-CH_3), 2.84 (2 H, dt, 5-H, $J_{4,5}$ 7 Hz, $J_{5,6}$ 1 Hz), 3.23 (3 H, s, N-CH_3), 3.52 (2 H, m, 3-H), 6.17 (1 H, m, 6-H), 6.22 (1 H, dd, 7-H?, $J_{7,8}$ 5 Hz, $J_{6,7}$ 2.5 Hz), and 6.43 (1 H, dd, 8-H?, $J_{6,8}$ 2 Hz) (Found: C, 81.2; H, 9.4; N, 8.3. $C_{11}H_{15}N$ requires C, 81.9; H, 9.4; N, 8.7%).

2,3,4,5-*Tetrahydro*-2-*methyl*-2-*phenylcyclopent*[c]*azepine* (**11b**) (0.30 g, 49%) was obtained from the methiodide (**6b**) (1.3 g, 2.7 mmol) in water (20 cm^3) and 10% aqueous sodium hydroxide (25 cm^3) and isolated like the preceding compound; it had m.p. 70 °C; $\nu_{max.}$(KCl) 3 090, 2 940, 1 600, and 1 450 cm^{-1}; δ($CDCl_3$) 2.08 (2 H, m, 4-H), 2.16 (3 H, s, CH_3), 3.08 (2 H, br t, 5-H), 3.65 (2 H, m, 3-H), 5.86 (1 H, dd, 6-H), 6.21 (2 H, m, 7- and 8-H), and 7.47 (5 H, m, C_6H_5) (Found: C, 85.7; H, 7.5; N, 6.4. $C_{16}H_{17}N$ requires C, 86.05; H, 7.7; N, 6.3%).

Acknowledgements

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