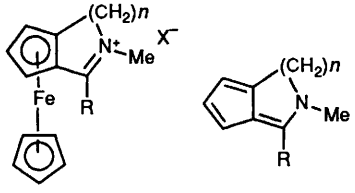
Ferrocene Derivatives. Part 25.[1] Their Use in the Synthesis of 5*H*-Cyclopenta-[*c*]quinolines and 5,6-Dihydro-5-azabenz[*e*]azulenes

Touhami Lanez and Peter L. Pauson *
Department of Pure and Applied Chemistry, Thomas Graham Building, University of Strathclyde, Cathedral Street, Glasgow G1 1XL

Arylation of ferrocene with *o*-nitro- and *o*-cyano-benzenediazonium salts leads smoothly to the *o*-nitro- and *o*-cyano-phenylferrocenes. These are reduced to *o*-ferrocenylaniline and *o*-ferrocenylbenzylamine respectively. Bischler–Napieralski cyclisation of the *N*-acyl derivatives of these amines proceeds with (partial) loss of iron to give the title compounds. The intermediate ferroceno-heterocycles, if isolated may be cleaved to the same products by exposure to diffuse daylight in aqueous acid solution. The liberation of 2,3,4,5-tetrahydrocyclopent[*c*]azepines by photolysis of the corresponding cyclopentadienyliron complexes in acidic medium is also briefly examined.

In our previous paper[1] we described the photolysis of the ferrocene derivatives (**1**) to yield dihydropyrindines (**2a**) or



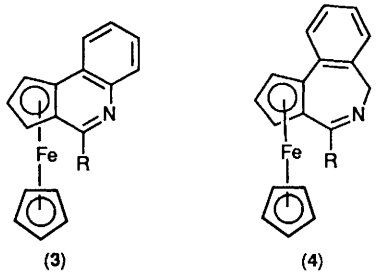
(**1**) (**2**)

a *n* = 2; **b** *n* = 3
R = H, Me, or Ph; X = I or BF_4

tetrahydrocyclopent[*c*]azepines (**2b**). Since we have so far failed in efforts to dehydrogenate these products or to generate fully aromatic precursors [*e.g.* (**1a**) less 2 H], we turned our attention to the benzo derivatives (**3**) and (**4**). We here describe their generation and decomplexation.

Results and Discussion

Although synthetic routes to compound (**3**) *via* ring expansion of the known ferrocenoindenone and ferrocenoindenol were



(**3**) (**4**)

a R = Me; **b** R = Ph

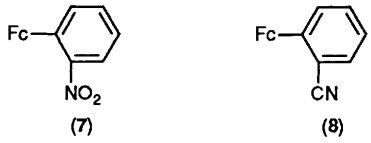
briefly examined, the successful method employed Bischler–Napieralski-type cyclisation of the amide precursors (**5b,c**) and (**6b,c**) analogous to the method previously used[1] to obtain the bicyclic complexes (**1**). These amides in turn were obtained by reduction and acylation of *o*-nitrophenyl- (**7**) and *o*-cyano-

(**5**) (**6**)

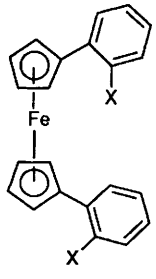
a R = H; **b** R = Ac; **c** R = Bz
Fc = Ferrocenyl

phenyl-ferrocene (**8**) respectively. The former compound (**7**) had previously been obtained[2] in very low yield; this was readily raised to 60% when the arylation of ferrocene with *o*-nitrobenzenediazonium chloride was carried out under the conditions recommended for the *m*- and *p*-isomers.[3] Significant quantities (*ca.* 10%) of 1,1′-bis(*o*-nitrophenyl)ferrocene (**9a**) were produced at the same time and this was converted into the diamide (**9c**). The arylation of ferrocene by *o*-cyanobenzenediazonium chloride also proceeded smoothly, only the monoarylated product (**8**) being isolated in a significant amount in this case.

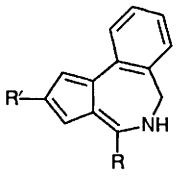
o-Ferrocenylbenzylacetamide (**6b**) readily underwent cyclis-



(**7**) (**8**)



(**9**)



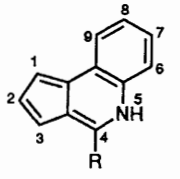
(**10**)

a; X = NO_2
b; X = NH_2
c; X = NHAc

a; R = Me, R′ = H
b; R = Ph, R′ = H
c; R = Me, R′ = CPh_3

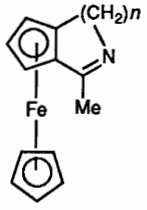
ation when heated with 'polyphosphate ester,' but the expected tricyclic ferrocene derivative (**4a**) was isolated in only 15% yield, the major product (57%) being the metal-free dihydroazabenz[*e*]azulene (**10a**). The assumption that the former is an intermediate in the formation of the latter product received support when the ferrocene (**4a**) was smoothly degraded on being stirred with dilute hydrochloric acid. However, this cleavage did not occur when daylight was excluded. Thus a photolytic cleavage of these tricyclic ferrocene derivatives occurs much more readily than that of the bicyclic systems (**1**) studied previously,[1] or the corresponding tertiary ammonium salts (see below). Under the conditions of the cyclisation reaction a thermal degradation of the ferrocenes (**4**) or possibly of precursors must also be occurring since the proportion of metal-free products (**10**) is hardly affected by exclusion of light. Thermal cleavage of α-ferrocenyl carbocations has been studied in the case of ferrocenyldiarylmethylium ions.[4]

Cyclisation of *o*-ferrocenylacetanilide (**5b**) proceeded similarly, but in this case the expected complex (**3a**) was present in an even smaller proportion, and its tendency to undergo degradation made its isolation so difficult that it proved more efficient to ensure its complete cleavage and to isolate only the metal-free cyclopentaquinoline (**11a**). This compound also resulted as the



(11)

a; R = Me
b; R = Ph

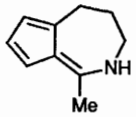


(12)

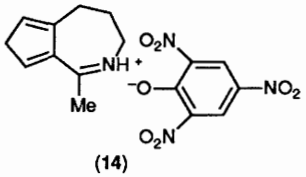
a; *n* = 2
b; *n* = 3

only product from cyclisation of the diamide (**9c**). Moreover, both benzamide derivatives (**5c**) and (**6c**) yielded only the metal-free products (**11b**) and (**10b**) respectively, without detectable amounts of the expected intermediate tricyclic ferrocene derivatives (**3b**) and (**4b**).

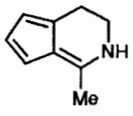
In the earlier work we had employed UV photolysis of the quaternary salts (**1**) which occurs smoothly in aqueous alkaline medium. In view of the facile degradation of the tricyclic systems described above, we have briefly investigated the photolysis of aqueous acid solutions of the imines (**12a,b**). The expected tetrahydrocyclopentazepine (**13**) was readily isolated as its picrate salt from such photolysis of the ferrocene (**12b**). The ^1H NMR spectrum of this salt suggests that protonation has taken place on the five-membered ring rather than on the nitrogen, and we tentatively formulate it as the iminium salt (**14**). Similar



(13)

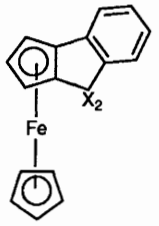


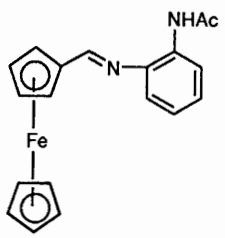
(14)



(15)

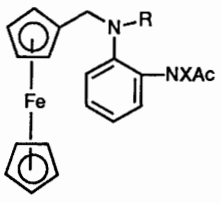
photolysis of the lower homologue (**12a**) yielded a product whose analysis and mass spectrum indicated the formula $C_{14}H_{15}N$ corresponding to the addition of the cyclopentadiene fragment of the precursor (**12a**) to the expected product (**15**). Although combination of these fragments by a Diels–Alder reaction could occur in several different ways, the NMR spectra did not correspond to any such formulation and the structure of the product remains unknown.



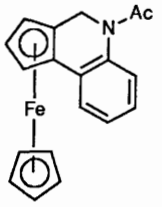


(19)

(16) X_2 = O
(17) X_2 = H, OH
(18) X_2 = NOH



(20)



(21)

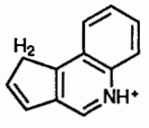
a; R = X = H
b; R = Ac, X = H
c; R = Ac, X = NO

As mentioned above, we initially attempted to obtain compounds of the type (**3**) *via* complex (**16**) or complex (**17**). An improved procedure for the preparation of the former is described in the Experimental section. An attempt to insert nitrogen into the middle ring of the alcohol (**17**) by a Schmidt reaction gave only the known[5] 'diferroceno[*b,b'*]bi-indenyl' on adding sodium hydroxide to an acidic solution of a precursor which was not isolated. Beckmann rearrangement of the oxime (**18**) of complex (**16**) was thought unlikely to proceed in the desired direction and was therefore abandoned when a single attempt to bring about reaction of the oxime (**18**) with toluene-*p*-sulphonyl chloride failed.

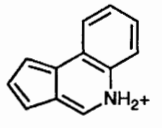
As an alternative possible precursor to compound (**3**) or related derivatives, we also prepared the amide (**20b**) by condensation of ferrocenecarbaldehyde with 2-aminoacetanilide to form the imine (**19**) followed by reduction and acetylation. However we failed in attempts to obtain the *N*-nitroso derivative (**20c**) which we would have expected to be convertible[2] into the heterocycle (**21**).

We also describe an attempt to dehydrogenate the dihydroazabenzazulene (**10a**) by reaction with triphenylmethyl tetrafluoroborate. This led instead to electrophilic substitution giving compound (**10c**) with the trityl group most probably in the 2-position.

NMR Spectra.—Whenever necessary, NH protons were identified by exchange with D_2O (or CD_3OD). When this was done for the picrate salt of the cyclopentaquinoline (**11a**), the signals tentatively assigned to 1-H and 2-H (see Experimental) also disappeared, suggesting that significant protonation also occurs at these positions in solution, giving *e.g.* structure (**22**),



(22)



(23)

although the principal species present clearly has two NH protons corresponding to structure (**23**). Reduced intensity of the signal due to the third proton on the 5-membered ring (tentatively 3-H) implies significantly slower protonation at this position. Analogous changes are observed for the other amines [(**10**), (**11**)] on protonation although the extent of *C*-protonation varies. But, as mentioned above, the picrate formed from the bicyclic amine (**13**) appears to be exclusively one of the *C*-protonated forms [tentatively (**14**)]; the clearest evidence for this is provided by the observation of four CH_2 signals in the ^{13}C NMR spectrum.

Experimental

All reactions were conducted under nitrogen. Alumina for chromatography was Spence's grade UG1 100 mesh which had been neutralised with ethyl acetate and dried at 150 °C. Light petroleum refers to the solvent of b.p. 40–60 °C unless otherwise stated. Ether refers to diethyl ether. Solutions were dried over anhydrous magnesium sulphate and evaporated under reduced pressure using a rotary evaporator.

(2-Nitrophenyl)ferrocene (**7**) *and 1,1′-Bis(2-nitrophenyl)ferrocene* (**9a**).—A solution of *o*-nitrobenzenediazonium chloride was prepared from *o*-nitroaniline (15.2 g, 0.11 mol) in an excess of 2M hydrochloric acid and sodium nitrite (8.0 g, 0.11 mol). This was filtered and added at once to a stirred solution of ferrocene (18.6 g, 0.1 mol) in ether (450 ml). Stirring was continued at room temperature until evolution of nitrogen ceased (*ca.* 3 h), whereupon the ether layer was separated, washed with water, dried, and evaporated. The residue was chromatographed on alumina. Light petroleum–ether (3:2) eluted compound (**7**) (18.4 g, 60%), purple crystals (from methanol), m.p. 114 °C (lit.,[2] 112–114 °C); ν_{max}(KCl) 3 098, 1 600, 1 510, 1 345, and 960 cm^{-1} (Found: C, 62.3; H, 4.1; N, 4.5. Calc. for $C_{16}H_{13}FeNO_2$: C, 62.6; H, 4.3; N, 4.6%). Further elution of the column with light petroleum–ether (3:7) gave *compound* (**9a**) (2.3 g, 10%), purple crystals (from methanol), m.p. 130–131 °C; ν_{max}(KCl) 3 098, 1 600, 1 510, and 1 350 cm^{-1}; $\delta(CDCl_3)$ 4.31 and 4.39 (each 4 H, d, C_5H_4) and 7.10–7.60 (8 H, m, C_6H_4) (Found: C, 61.3; H, 3.6; N, 6.4. $C_{22}H_{16}FeN_2O_4$ requires C, 61.7; H, 3.7; N, 6.5%). The use of 4 mol of *o*-nitroaniline per mol of ferrocene raised the yield of this product (**9a**) to 35–40%.

2-Ferrocenylbenzonitrile (**8**).—A cold solution of 2-cyanobenzenediazonium sulphate was prepared from 2-cyanoaniline (anthranilonitrile) (4.0 g, 34 mmol) in an excess of 2M sulphuric acid and an aqueous solution of sodium nitrite (2.46 g, 34 mmol) and added dropwise to a stirred solution of ferrocene (6.28 g, 34 mmol) in ether (100 ml). The mixture was stirred for 3 h after which the ether layer was separated, washed with water, dried, and evaporated. The residue was chromatographed using dichloromethane–light petroleum (3:2) to elute the *product* (**8**) (5.72 g, 59%), orange–red needles (from ethanol), m.p. 63–64 °C; ν_{max}(KCl) 3 095, 2 220, 1 600, 1 105, 1 002, and 760 cm^{-1}; $\delta(CDCl_3)$ 4.15 (5 H, s, C_5H_5), 4.45 and 4.95 (each 2 H, m, C_5H_4), and 7.15–7.70 (4 H, br m, C_6H_4) (Found: C, 70.95; H, 4.5; N, 4.8. $C_{17}H_{13}FeN$ requires C, 71.1; H, 4.6; N, 4.9%). Further elution with the same solvent mixture gave a few orange–red crystals (from aqueous ethanol), m.p. 134–135 °C; ν_{max}(KCl) 3 095, 2 220, 1 600, and 760 cm^{-1}, presumably 1,1′-bis(2-cyanophenyl)-ferrocene.

2-Ferrocenylaniline (**5a**).—The reduction method of Neilson, Wood, and Wylie[6] was used. Palladium on charcoal (10%; 50 mg) was suspended in water (10 ml) and sodium borohydride (0.12 g, 3.26 mmol) in water (2.5 ml) was added. A slow stream of nitrogen was bubbled through the mixture and a solution of (2-nitrophenyl)ferrocene (**7**) (0.5 g, 1.63 mmol) in methanol (25 ml) (supercooled solution) was added dropwise. After addition was completed, the reaction mixture was stirred for 15 min at room temperature and then filtered. The filtrate was acidified with 2M hydrochloric acid to destroy excess of borohydride and then basified with 2M sodium hydroxide and extracted with ether. Evaporation of the dried extract left *2-ferrocenylaniline* (**5a**) (0.43 g, 95%), as an orange oil, b.p. 147 °C/0.001 Torr; ν_{max}(film) 3 440, 3 345, 1 610, and 820 cm^{-1}; $\delta(CDCl_3)$ *ca.* 4.10 (2 H, br s, NH_2), 4.17 (5 H, s, C_5H_5), 4.34 and 4.57 (each 2 H, m, C_5H_4), and 6.72 and 7.00–7.40 (each 2 H, m, C_6H_4) (Found: C, 69.4; H, 5.6; N, 5.0. $C_{16}H_{15}FeN$ requires C, 69.3; H, 5.45; N, 5.05%).

1,1′-Bis(2-aminophenyl)ferrocene (**9b**).—Reduction of 1,1′-bis(2-nitrophenyl)ferrocene (**9a**) (4.61 g, 11 mmol) followed the procedure of the preceding experiment and yielded the *diamine* (**9b**) (3.74 g, 95%) as orange–yellow plates (from ethanol), m.p. 121 °C; ν_{max}(KCl) 3 390, 3 320, 1 605, and 750 cm^{-1}; $\delta(CDCl_3)$ 4.05 (4 H, br s, NH_2), 4.26 and 4.48 (each 4 H, m, C_5H_4), and 6.55 and 7.05 (each 4 H, m, C_6H_4) (Found: C, 71.4; H, 5.2; N, 7.5. $C_{22}H_{20}FeN_2$ requires C, 71.75; H, 5.5; N, 7.5%).

2-Ferrocenylbenzylamine (**6a**).—To lithium aluminium hydride (0.23 g, 6.10 mmol) in dry ether (5 ml), a solution of 2-ferrocenylbenzonitrile (**8**) (1.17 g, 4.07 mmol) in ether (8 ml) was added dropwise and the mixture then stirred at room temperature overnight. After addition of moist ether to destroy excess of hydride, and then water, the mixture was filtered and the ether layer dried and evaporated. The residual *amine* (**6a**) (0.90 g, 76%) was distilled, b.p. 130 °C/0.05 Torr; ν_{max}(film) 3 370, 3 300, 3 090, 2 925, 1 600, 1 103, and 1 002 cm^{-1}; $\delta(CDCl_3)$ 1.37 (2 H, br s, NH_2), 3.89 (2 H, s, CH_2), 4.15 (5 H, s, C_5H_5), 4.30 and 4.47 (each 2 H, m, C_5H_4), 7.25 (3 H, m), and 7.78 (1 H, m, C_6H_4) (Found: C, 70.1; H, 5.9; N, 4.9. $C_{17}H_{17}FeN$ requires C, 70.1; H, 5.9; N, 4.8%).

2-Ferrocenylacetanilide (**5b**).—The amine (**5a**) (0.3 g, 0.94 mmol) when stirred in toluene (5 ml) with acetic anhydride (0.2 g, 1.88 mmol) for 15 min gave the *amide* (**5b**) (0.32 g, 92%) as orange-yellow needles (from ethanol), m.p. 108 °C; ν_{max}(KCl) 3 350, 3 080, 1 685, 1 580, 812, and 755 cm^{-1}; $\delta(CDCl_3)$ 2.26 (3 H, s, CH_3), 4.21 (5 H, s, C_5H_5), 4.42 and 4.50 (each 2 H, m, C_5H_4), 7.25 (3 H, m), and 8.22 (2 H, m, C_6H_4 and NH) (Found: C, 67.8; H, 5.25; N, 4.3. $C_{18}H_{17}FeNO$ requires C, 67.7; H, 5.4; N, 4.4%).

2-Ferrocenylbenzanilide (**5c**).—The amine (**5a**) (2 g, 7.2 mmol) in toluene (8 ml) and pyridine (1.5 g, 11 mmol) was stirred with benzoyl chloride (0.87 g, 11 mmol) for 20 min. The solution was filtered, poured into water, and the toluene layer separated, washed twice with water, dried and concentrated. Addition of light petroleum precipitated the *amide* (**5c**) (2.4 g, 87%) as a fine crystalline powder, m.p. 97–98 °C; ν_{max}(KCl) 3 290, 1 645, 1 600, 1 580, 755, and 715 cm^{-1}; $\delta(CDCl_3)$ 4.13 (5 H, s, C_5H_5), 4.40 and 4.49 (each 2 H, m, C_5H_4), 7.13–7.90 (9 H, m, C_6H_4 and C_6H_5), and 8.75 (1 H, br s, NH) (Found: C, 72.1; H, 4.9; N, 3.6. $C_{23}H_{19}FeNO$ requires C, 72.4; H, 5.0; N, 3.7%).

1,1′-Bis(2-acetamidophenyl)ferrocene (**9c**).—To the diamine (**9b**) (0.56 g, 1.52 mmol) in acetic anhydride (0.62 g, 6.1 mmol) and toluene (6 ml), pyridine (0.48 g, 6.1 mmol) was added, and the mixture was stirred for 0.5 h and then poured into water. The organic layer was separated, dried, and evaporated to give the *diacetyl derivative* [**9c**) (0.65 g, 95.5%) as orange-yellow plates (from ethanol), m.p. 195 °C; ν_{max}(KCl) 3 220, 1 640, 1 600, and 755 cm^{-1}; $\delta(CDCl_3)$ 2.05 (6 H, s, CH_3), 4.34 and 4.45 (each 4 H, m, C_5H_4), and 6.85–7.40 and 7.70–8.00 (10 H, m, C_6H_4 + NH) (Found: C, 69.2; H, 5.1; N, 6.2. $C_{26}H_{24}FeN_2O_2$ requires C, 69.0; H, 5.35; N, 6.2%).

N-*Acetyl*-2-*ferrocenylbenzylamine* (**6b**).—Acetic anhydride (2.79 g, 27 mmol) was slowly added to a stirred solution of 2-ferrocenylbenzylamine (**6a**) (4.0 g, 13 mmol) in dry toluene (25 ml) and the mixture stirred for 20 min. It was then poured into water; the toluene layer was separated, dried, and evaporated to leave the N-*acetyl derivative* (**6b**) (4.56 g, 100%) as orange needles [from toluene–light petroleum (b.p. 30–40 °C)], m.p. 98 °C; ν_{max}(KCl) 3 295, 3 085, 1 640, 1 103, 1 000, and 765 cm^{-1}; $\delta(CDCl_3)$ 1.90 (3 H, s, CH_3), 4.17 (5 H, s, C_5H_5), 4.34 and 4.43 (each 2 H, m, C_5H_4), 4.53 (2 H, d, CH_2),* 5.62 (1 H, br s, NH), 7.25 (3 H, m), and 7.80 (1 H, m, C_6H_4) (Found: C, 68.3; H, 5.6; N, 4.1. $C_{19}H_{19}FeNO$ requires C, 68.5; H, 5.75; N, 4.2%).

N-*Benzoyl*-2-*ferrocenylbenzylamine* (**6c**).—Pyridine (0.41 g, 5.2 mmol) and benzoyl chloride (0.73 g, 5.2 mmol) were added to a solution of the amine (**6a**) (1.0 g, 3.4 mmol) in toluene (5 ml) and the mixture was heated to 80 °C for 1 h. It was then poured into water; the toluene layer was separated, dried, and evaporated. The N-*benzoyl derivative* [**6c**) (0.85 g, 62%) was obtained as yellow plates (from toluene), m.p. 198 °C; ν_{max}(KCl) 3 335, 1 635, 1 103, 1 000, 810, and 695 cm^{-1} (Found: C, 73.3; H, 5.3; N, 3.4. $C_{24}H_{21}FeNO$ requires C, 72.9; H, 5.35; N, 3.5%).

Cyclisation Reactions

Cyclisation of N-*Acetyl*-2-*ferrocenylbenzylamine* (**6b**).—The amide (**6b**) (3.5 g, 10.5 mmol) in dry toluene (80 ml) was slowly added to a well-stirred solution of 'polyphosphate ester' [7] (21 g) in toluene (50 ml). The mixture was heated to 80 °C for 1 h during which the colour changed from yellow to deep purple. It was then poured into 5% hydrochloric acid and the organic layer removed. The aqueous layer was made alkaline with 2M sodium hydroxide and extracted with toluene. The dried extract was evaporated and the residue chromatographed on alumina. Ether first eluted 5,6-*dihydro*-4-*methyl*-5-*azabenzo*[e]*azulene* (**10a**) (1.2 g, 57%) as bright yellow plates (from ethanol), m.p. 153–154 °C; ν_{max}(KCl) 3 290, 1 600, 1 565, 1 340, 755, and 730 cm^{-1}; $\delta_H(CDCl_3)$ 2.37 (3 H, s, CH_3), 4.20 (2 H, d, J_{CH_2-NH} 5.3 Hz, CH_2), 5.80 (1 H, br s, NH), 6.53 (1 H, m, 1-H), 6.70 (1 H, m, 2-H), 6.89 (1 H, m, 3-H),† 7.13 (2 H, m, 7-H, 8-H), 7.28 (1 H, m, 9-H), and 7.62 (1 H, d, $J_{9,10}$ 7.7 Hz, 10-H); $\delta_C(CDCl_3)$ 21.67 (CH_3), 51.03 (CH_2), 119.34, 119.97, 121.19, 125.48, 127.42, 127.47, and 128.24 (each CH), 117.07, 129.34, 131.98, 137.84, and 157.93 (Found: C, 86.3; H, 6.9; N, 7.2. $C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.2%).

Further elution with ether gave the *complex* (**4a**) (0.52 g, 15%), purple crystals (from ether–light petroleum, 4:6), m.p. 112 °C; ν_{max}(KCl) 3 080, 2 925, 1 615, 815, and 760 cm^{-1}; $\delta(CDCl_3)$ 2.44 (3 H, s, CH_3), 4.08 (5 H, s, C_5H_5), 4.16–4.95 (5 H, m, C_5H_3 and CH_2), 7.24 (3 H, m), and 7.65 (1 H, m, C_6H_4) (Found: C, 71.6; H, 5.5; N, 4.1. $C_{19}H_{17}FeN$ requires C, 72.4; H, 5.4; N, 4.4%).

A solution of this complex (**4a**) (0.2 g) in 2M hydrochloric acid (5 ml) was unchanged after being stirred in the dark for 24 h, but decomposed to yield the metal-free amine (**10a**) within 0.5 h in diffuse daylight.

The base (**10a**) was further characterised as its *picrate*, yellow crystals, m.p. 126 °C (from aqueous ethanol); ν_{max}(KCl) 3 080, 2 925, 1 615, 815, and 760 cm^{-1}; $\delta(CDCl_3)$ 2.78 (3 H, s, CH_3), 3.80 (2 H, s, NH_2), 4.63 (2 H, br s at 292 K, v br at 273 K but fairly sharp at 323 K, CH_2), 7.28 (3 H, m, 1-H–3-H), 7.60 (1 H, m), and 7.69 (3 H, m, C_6H_4), and 8.90 (2 H, s, C_6H_2 of picrate). The mass spectrum showed fragment ions at *m/z* 195.1055 (base peak; Calc. for $C_{14}H_{13}N$: 195.1048) and 180.0815 ($C_{13}H_{10}N$: 180.0813). (Found: C, 56.5; H, 3.8; N, 13.0. $C_{20}H_{19}N_4O_5$ requires C, 56.6; H, 3.8; N, 13.2%).

5,6-*Dihydro*-4-*phenyl*-5-*azabenz*[*e*]*azulene* (**10b**).—Using the procedure of the preceding experiment, cyclisation of *N*-benzoyl-2-ferrocenylbenzylamine (**6c**) (3.5 g, 8.85 mmol) using 'polyphosphate ester' (21 g) gave the *metal-free base* (**10b**) (0.68 g, 52%) as the only isolable product; orange–red crystals, m.p. 178–179 °C (from ethanol); ν_{max}(KCl) 3 365, 1 600, 1 580, 1 550, 1 530, and 1 415 cm^{-1}; $\delta(CDCl_3)$ 4.43 (2 H, d, J_{CH_2NH} 6 Hz, CH_2), 5.82 (1 H, br s, NH), 6.28 (1 H, dd, $J_{1,2}$ 4.6, $J_{1,3}$ 1.8 Hz, 1-H), 6.53 (1 H, dd, $J_{2,3}$ 2.8 Hz, 2-H), 6.97 (1 H, dd, 3-H),† and 7.15–7.71 (9 H, m, 7-H–10-H + C_6H_5) (Found: C, 88.8; H, 5.9; N, 5.3. $C_{19}H_{15}N$ requires C, 88.7; H, 5.9; N, 5.4%).

Cyclisation of 2-*Ferrocenylacetanilide* (**5b**).—This amide (**5b**) (0.40 g, 1.25 mmol) in dry toluene (5 ml) was added to a stirred solution of 'polyphosphate ester' [7] (3 g) in toluene (5 ml) and the mixture was heated to 80 °C for 2 h and then cooled, poured into water, and separated. The aqueous layer was made alkaline with 2M sodium hydroxide and extracted with toluene. Evaporation of the dried extract left a brown oil, shown by microanalysis and mass spectroscopy to be a mixture of the expected *complex* (**3a**) and the *metal-free base* (**11a**) (Found: C, 84.6; H, 7.3; N, 5.5%; *M*, 301.0563 and 181.0827. $C_{18}H_{15}FeN$ requires C, 71.8; H, 5.0; N, 4.65%; *M*, 301.0553. $C_{13}H_{11}N$ requires C, 86.15; H, 6.1; N, 7.7%; *M*, 181.0891). Separation by column chromatography was unsuccessful because of the continuing decomposition of the iron compound (**3a**). This was brought to completion by stirring the mixture in diffuse daylight with 5% aqueous hydrochloric acid for 30 min. The amine (**11a**) (0.11 g, 53%) was isolated from the resulting solution as its *picrate*, yellow plates, m.p. 182–183 °C (from ethanol); ν_{max}(KCl) 3 080, 2 910, 1 605, 725, and 710 cm^{-1}; $\delta(CDCl_3)$ 3.03 (3 H, s, CH_3), 3.85 (2 H, s, NH_2), 7.55 (1 H, d, *J* 5.5 Hz, 1-H), 7.68 (1 H, d, 2-H),† 7.83 and 7.96 (each 1 H, t overlapping m, 7-H, 8-H, and 3-H), 8.26 and 8.39 (each 1 H, d, 6-H, 9-H), and 8.95 (2 H, s, C_6H_2 of picrate) (Found: C, 55.4; H, 3.2; N, 13.4. $C_{19}H_{14}N_4O_7$ requires C, 55.6; H, 3.4; N, 13.65%).

Cyclisation of 1,1′-*Bis*(2-*acetamidophenyl*)*ferrocene* (**9c**).—The diamide (**9c**) (1.0 g, 2.2 mmol) was cyclised with 'polyphosphate ester' (6 g) in toluene (8 ml) in the manner of the preceding cyclisation reactions. The only isolable product was the cyclopentaquinoline (**11a**) (0.46 g, 50%); its MS showed a base peak at *m/z* 181.0882 (Calc. for $C_{13}H_{11}N$: 181.0891) and its picrate was identical with the sample from the preceding experiment.

4-*Phenyl*-5H-*cyclopenta*[c]*quinoline* (**11b**).—The benzamide derivative (**5c**) (2.5 g, 6.5 mmol) was cyclised with 'polyphosphate ester' (10 g) in toluene (25 ml) at 80 °C for 2 h. After reaction and work-up by the above general method the product (**11b**) (0.86 g, 53%) was obtained as a deep red oil and characterised as its *picrate*, yellow crystals, m.p. 165 °C (from aqueous methanol); ν_{max}(KCl) 3 080 and 1 605 cm^{-1}; $\delta(CDCl_3)$

* The NH group of this compound gives rise to an unresolved broad peak, but nevertheless splits the adjacent CH_2 to give a doublet. The highfield portion of this doublet partly overlaps the C_5H_4 signal at 4.43 in $CDCl_3$ but is well separated from this in $C_6D_5CD_3$. In this solvent at 303 K the peaks appear at δ 1.41(CH_3), 3.91 (C_5H_5), 4.01 and 4.23 (each 2 H, t, C_5H_4), 4.44 (d, CH_2), *ca.* 4.52 (br s, NH), 6.9–7.1 (C_6H_4 plus solvent), and 7.64 (1 H, C_6H_4). The CH_2 doublet is now so close to the NH signal that the doublet is unsymmetrical, leaning strongly towards the NH signal, but when the solution is cooled these signals separate until at 213 K a symmetrical doublet is observed at δ *ca.* 4.52 with the broad NH signal at δ 5.4.

† Probable assignments for 1-, 2-, and 3-H; neither the splitting patterns nor the available analogies suffice for definitive identification of these peaks.

3.93 (2 H, s, NH_2), 7.45 (3 H, m), 7.78 (4 H, m, 1-H, 2-H, and C_6H_5), 7.58 (1 H, d, 3-H), 7.88 (1 H, t), 8.03 (1 H, t, 7-H, 8-H), 8.33 (1 H, d), 8.73 (1 H, d, 6-H, 9-H), and 8.79 (2 H, s, C_6H_2 of picrate) (Found: C, 60.7; H, 3.05; N, 11.5. $C_{24}H_{16}N_4O_7$ requires C, 61.0; H, 3.4; N, 11.8%).

Photolysis

2,3,4,5-*Tetrahydro*-1-*methylcyclopent*[c]*azepine* (**13**).—The imine (**12b**) (2.0 g, 7.5 mmol) in 10% sulphuric acid (150 ml) was irradiated for 6 h during which the initial deep purple colour of the solution changed to yellow. The solution was filtered and extracted with ether. The aqueous layer was made basic and re-extracted with ether and this extract was dried and evaporated. The residue, a mobile yellow oil (600 mg, 55%), was shown to contain the unstable fulvene (**13**) by conversion into its *picrate* (**14**?), yellow crystals, m.p. 158 °C (from aqueous methanol ν_{max}(KCl) 3 095, 2 910, 1 630, 1 610, 1 435, and 1 360 cm^{-1}; $\delta(CDCl_3)$ 2.23 (2 H, m, 4-H), 2.72 (3 H, s, CH_3), 3.12 (2 H, m, 5-H), 3.55 (2 H, t, 7-H), 3.88 (2 H, m, 3-H), 6.75 (1 H, d, 6-H), 7.10 (1 H, d, *J* 5.1 Hz, 8-H), and 8.88 (2 H, s, C_6H_2 of picrate) (Found: C, 51.4; H, 4.3; N, 15.3. $C_{16}H_{16}N_4O_7$ requires C, 51.1; H, 4.3; N, 14.9%).

Photolysis of Compound (**12a**).—A solution of the imine (**12a**) (1.0 g, 3.9 mmol) in 10% sulphuric acid was irradiated for 6 h. Work-up as in the preceding experiment gave an orange–yellow oil (0.47 g) which yielded a yellow *picrate*, m.p. 265 °C (decomp.) (from aqueous ethanol); ν_{max}(KCl) 3 320, 1 600, 1 435, 1 305, and 1 200 cm^{-1}; $\delta[(CD_3)_2SO]$ 1.36 (1 H, m), 1.89 (2 H, s), 2.22 (1 H, m), 2.28 (3 H, s), 3.15 (1 H, m), 3.67 (3 H, m), 5.10 (1 H, m), 5.29 (1 H, m), 7.65 (1 H, d), 8.51 (1 H, d), and 8.57 (2 H, s, C_6H_2 of picrate); major peaks in the mass spectrum at *m/z* 197.1147 (Calc. for $C_{14}H_{15}N$: 197.1164), 196. 1118 ($C_{14}H_{14}N$: 196.1126), 183.1015 ($C_{13}H_{12}N$: 183.1003), 132.0772 ($C_{10}H_{10}$: 132.0850) and 131.0695 ($C_{10}H_9$: 131.0771) (Found: C, 56.4; H, 4.2; N, 13.3. $C_{20}H_{18}N_4O_7$ requires C, 56.3; H, 4.3; N, 13.1%).

Miscellaneous

η-*Cyclopentadienyl*{(1,2,3,3a,8a-η)-8-*oxocyclopent*[a]-*indenyl*}*iron* (**16**).—A solution of 2-ferrocenylbenzoic acid (0.5 g, 1.56 mmol) in dry toluene (6 ml) was added to 'polyphosphate ester'[7] (3 g) in toluene (10 ml) and the mixture stirred at room temperature for 1 h. It was then poured into ice–water and the organic layer was separated, washed with water and with 2M sodium hydroxide, dried, and evaporated. The residual ketone (**16**) (0.19 g, 42%) formed purple–red needles, m.p. 102–103 °C (from light petroleum) (lit.,[5] m.p. 104–105 °C); ν_{max}(KCl) 3 065, 2 925, 1 700, 1 605, 765, and 720 cm^{-1}; $\delta(CDCl_3)$ 4.18 (5 H, s, C_5H_5), 5.00 (3 H, m, C_5H_3), and 7.50 (4 H, m, C_6H_4) (Found: C, 71.2; H, 4.4. Calc. for $C_{17}H_{12}FeO$: C, 70.9; H, 4.2%).

η-*Cyclopentadienyl*{(1,2,3,3a,8a-η)-8-*hydroxyiminocyclopent*[a]*indenyl*}*iron* (**18**).—The preceding ketone (**16**) (0.95 g, 3.3 mmol) in ethanol (4 ml) and pyridine (1.5 ml) was heated under reflux with hydroxylamine hydrochloride (0.25 g, 3.6 mmol) for 2 h. Removal of solvent and crystallisation from toluene–hexane gave the *oxime* (**18**) (0.80 g, 80%) as purple crystals, m.p. 166 °C; ν_{max}(KCl) 3 240, 1 630, 1 600, and 1 110 cm^{-1}; $\delta(CDCl_3)$ 4.01 (5 H, s, C_5H_5), 4.58, 4.71, and 5.08 (each 1 H, m, C_5H_3), 7.11 and 7.33 (4 H, m, C_6H_4), and 7.58 (1 H, m, OH) (Found: C, 67.5; H, 4.2; N, 4.5. $C_{17}H_{13}FeNO$ requires C, 67.4; H, 4.3; N, 4.6%).

η-*Cyclopentadienyl*{(1,2,3,3a,8a-η)-8-*hydroxycyclopent*[a]-*indenyl*}*iron* (**17**).—This compound, prepared from the ketone (**16**) by reduction with sodium borohydride,[5] formed yellow plates, m.p. 93 °C [from ether–light petroleum (3:7)] (lit.,[5] m.p. 90–91 °C); ν_{max}(KCl) 3 560, 3 420, 1 610, 760, and 730 cm^{-1}; $\delta(CDCl_3)$ 2.18 (1 H, d, OH), 4.20 (5 H, s, C_5H_5), 4.42 (3 H, m, C_5H_3), 5.20 (1 H, d, C*H*OH), and 7.33 (4 H, m, C_6H_4) (Found: C, 70.3; H, 5.0. Calc. for $C_{17}H_{14}FeO$: C, 70.4; H, 4.8%).

'Diferroceno[b,b']*bi-indenyl'*.—Concentrated sulphuric acid (1.2 ml) was added dropwise to an ice-cold suspension of sodium azide (0.3 g, 4.4 mmol) in chloroform and the mixture was stirred for 10 min. A solution of complex (**17**) (0.5 g, 1.72 mmol) in chloroform (12 ml) was then added at room temperature over 5 min and stirring continued for 20 min. The mixture was then poured into a mixture of ice and aqueous titanium(III) chloride. The aqueous layer was separated and made alkaline with 2M sodium hydroxide to give a brown solid (0.72 g, 77%) which was isolated by extraction into ether and then drying and evaporation of the extract. Recrystallisation of the residue from ether gave orange–brown crystals which did not melt below 360 °C and whose other properties also corresponded with those reported[5] for 'diferroceno[b,b']biindenyl'; ν_{max}(KCl) 3 085, 1 600, 1 105, 760, and 745 cm^{-1}; $\delta(CDCl_3)$ 3.40 (2 H, d, methine H), 3.75 (10 H, s, C_5H_5), 3.85, 4.25, and 4.60 (each 2 H, m, C_5H_3), and 7.05 and 7.35 (8 H, m, C_6H_4) (Found: C, 74.5; H, 4.5. Calc. for $C_{34}H_{26}Fe_2$: C, 74.7; H, 4.8%).

2-(*Ferrocenylmethyleneamino*)*acetanilide* (**19**).—Ferrocenecarbaldehyde (4.0 g, 18.6 mmol) and 2-aminoacetanilide[8] (5.6 g, 37.3 mmol) were heated together in ethanol (15 ml) under reflux until a clear solution resulted (*ca.* 15 min) and then left in a stoppered flask for 8 d. The orange product was filtered off, washed with cold ethanol, dried, and recrystallised from hexane to give orange–red needles of *compound* (**19**) (6.13 g, 95%), m.p. 99.5–100 °C; ν_{max}(KCl) 3 360, 1 690, 1 615, 1 590, 1 430, and 1 310 cm^{-1}; $\delta(CDCl_3)$ 2.05 (3 H, s, CH_3), 4.15 (5 H, s, C_5H_5), 4.55 and 4.85 (each 2 H, m, C_5H_4), 7.1 (3 H, m) and 8.45 (2 H, m, C_6H_4 and NH) (Found: C, 66.0; H, 5.3; N, 8.1. $C_{19}H_{18}FeN_2O$ requires C, 65.9; H, 5.2; N, 8.1%).

2-(*Ferrocenylmethylamino*)*acetanilide* (**20a**).—Sodium borohydride (18.2 mg, 0.5 mmol) was added in small portions to a solution of the preceding imine (**19**) (140 mg, 0.4 mmol) in methanol (5 ml) and the mixture was stirred at room temperature for 2 h. After removal of solvent, the residue was shaken with 2M hydrochloric acid and the resulting solution made alkaline with 2M sodium hydroxide and extracted with dichloromethane. The dried extract was evaporated and the residue crystallised from ethanol. The *amine* (**20a**) (0.12 g, 86%) formed yellow plates, m.p. 148–149 °C; ν_{max}(KCl) 3 410, 3 250, 1 650, 1 600, 1 510, and 740 cm^{-1} (Found: C, 65.3; H, 5.5; N, 8.1. $C_{19}H_{20}FeN_2O$ requires C, 65.5; H, 5.8; N, 8.0%).

2-(*Ferrocenylmethylacetamido*)*acetanilide* (**20b**).—The amine (**20a**) (0.7 g, 2.0 mmol) was dissolved in acetic anhydride (6 ml) at room temperature and stirred. After 15 min a yellow precipitate had formed which was filtered off, washed with water until free of acetic anhydride, dried, and recrystallised from ethanol to give the *diamide* (**20b**) (0.73 g, 93%) as yellow plates, m.p. 195 °C; ν_{max}(KCl) 3 300, 1 690, 1 650, 1 590, 1 535, and 1 295 cm^{-1}; $\delta(CDCl_3)$ 1.70 (3 H, s, CH_3), 1.82 (3 H, s, CH_3), 3.86 (2 H, m, CH_2), 4.15 and 4.40 (9 H, m, C_5H_5 and C_5H_4), 6.75 (1 H, s, NH), and 7.05–7.40 and 8.16 (4 H, m, C_6H_4) (Found: C, 64.3; H, 5.95; N, 7.05. $C_{21}H_{22}FeN_2O_2$ requires C, 64.6; H, 5.7; N, 7.2%).

5,6-*Dihydro*-4-*methyl*-2(?)-(*triphenylmethyl*)-5-*azabenz*[e]-*azulene* (**10c**).—To a solution of compound (**10a**) (130 mg, 0.66 mmol) in dry dichloromethane (5 ml) was added a solution of triphenylmethyl tetrafluoroborate (660 mg, 1.98 mmol) in the same solvent (12 ml) and the mixture stirred at room

temperature for 4 d. After removal of solvent, the residue was chromatographed on alumina, eluting with ether. Evaporation of ether gave very bright yellow crystals (0.24 g, 82%) of the *product* (**10c**), m.p. 207 °C (decomp.) (from ethanol); ν_{max}(KCl) 1 565, 1 485, 1 440, 1 320, 1 300, and 700 cm^{-1}; $\delta(CDCl_3)$ 2.22 (3 H, s, CH_3), 4.22 (2 H, d, J_{CH_2-NH} 5 Hz, CH_2), 5.48 (1 H, br s, NH), 6.28 (1 H, d, $J_{1,3}$ 2.2 Hz, 1-H), 6.56 (1 H, d, 3-H),* and 7.10–7.44 (19 H, m, 7-H–10-H, and C_6H_5) (Found: C, 89.7; H, 6.3; N, 3.0. $C_{33}H_{27}N$ requires C, 90.6; H, 6.2; N, 3.2%).

Acknowledgements

The authors thank the Algerian Ministry of Higher Education for a studentship (T. L.).

References

1 Part 24, I. U. Khand, T. Lanez, and P. L. Pauson, *J. Chem. Soc., Perkin Trans. 1*, 1989, 2075.

2 G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 1955, 367.

3 A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, 1954, **97**, 459; A. N. Nesmeyanov, E. G. Perevalova, and R. V. Golovnya, *ibid.*, 1954, **99**, 539; A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and L. S. Shilovtseva, *ibid.*, 1955, **102**, 535.

4 N. Cully, W. D. Quail, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1148.

5 M. Cais, A. Modiano, and A. Raveh, *J. Am. Chem. Soc.*, 1965, **87**, 5607.

6 T. Neilson, H. C. S. Wood, and A. G. Wylie, *J. Chem. Soc.*, 1962, 371.

7 Y. Kanaoka, E. Sato, O. Yonemitsu, and Y. Ban, *Tetrahedron Lett.*, 1964, 2419; *cf.* L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1967, p. 892.

8 C. H. Roeder and A. R. Day, *J. Org. Chem.*, 1941, **6**, 25.

Paper 0/00604A
Received 9*th February* 1990
Accepted 21*st February* 1990

* See footnote † on p. 2440.