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Cyclopenta[*a*]quinolizine: A Novel Pseudoazulene with a Bridgehead Nitrogen Atom

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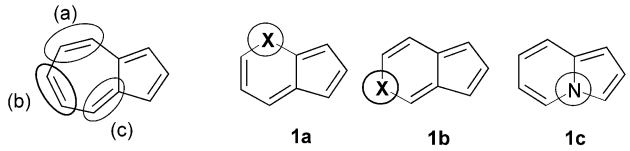
Cyclopenta[*a*]quinolizine, a novel tricyclic pseudoazulene, was prepared by reaction of cyclopentadienyllithium with oxazolo[3,2-*a*]pyridinium or substituted pyridinium salts. Structural analysis (X-ray analysis, NMR and UV spectroscopy) and DFT calculations confirm its highly dipolar nature (due to delocalization of the negative charge around the five-membered ring) combined with partial localization of bonds in both six-membered rings.

Introduction

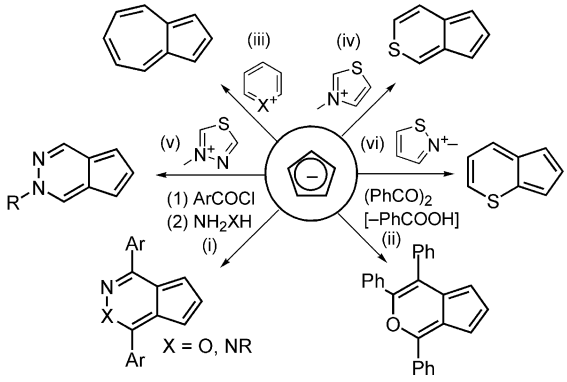
Pseudoazulenes **1** represent an interesting class of dipolar aromatic molecules that are π-isoelectronic to azulene, where the lone pair of electrons of a heteroatom in the six-membered ring is formally derived from one of double bonds at the seven-membered ring of the parent azulene scaffold (Scheme 1).



Scheme 1.

This structural analogy leads to similar properties: the aromaticity of **1**, their π-excessive character, and even the reactivity of pseudoazulenes strongly resemble those of azulenes; they all easily undergo C-protonation and electrophilic substitution at the five-membered ring. (Indolizines **1c** also following these rules, but they are usually considered separately from families **1a**,**b**.) Several old reviews[1] summarize the synthesis and the chemistry of pseudoazulenes, although the data on parent bicycles **1a**,**b** are less representative than for their benzo and aza derivatives (like stable anhydrobases of azafluorenes or azaindoles). Only few fully aromatic structures of the type **1b** exist in nature, for example, iridoids of plants (X = O[2]) or tautomers of 2*H*-pyrindine (X = NH, discovered in oils[3]), whereas partially saturated pseudoazulenes occur more frequently among many natural products. In modern material science, attention to pseudoazulenes is quickly growing due to their interesting optical properties.[4] Because scaffolds **1a**,**b** are isostructural to purines, their appearance among the structures of drug candidates[5] is not surprising.

The synthesis of pseudoazulenes **1a**,**b** frequently involves attachment of a new azine ring to five-membered carbocycles (e.g., condensations by using cyclopentanone or various cycloadditions to fulvenes and cyclopentadiene[1]). One elegant approach to build scaffolds **1a**,**b** is the reaction of the cyclopentadienyl anion (CPA) with open-chain reagents or their cyclic equivalents – heterocyclic salts (Scheme 2). In this strategy, the novel azine ring is built by stepwise condensations (Scheme 2, i[6] and ii[7]) or one-pot ring transformations of (usually sulfur-containing) azolium salts (Scheme 2, iv,[8] v,[9] and vi[10]).



Scheme 2.

In Scheme 2, reactions iv–vi, the CPA molecule serves as a 1,2-binuleophilic counterpart to the 1,4-bielectrophilic azolium salts, resembling Hafner azulene synthesis (Scheme 2, iii) from CPA and 1,5-bielectrophilic azinium salts (X = O, NR) or their open-chain equivalents.[11] Although this method could be expanded to a broader set of heterocyclic salts, we were unable to find more such examples in the literature.

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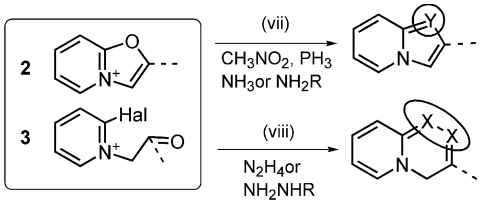
During the past decade we have extensively studied the reactivity of oxazolo[3,2-*a*]pyridinium salts **2** and their monocyclic precursors: 2-halopyridinium salts **3**.[12] It was shown that in reactions with many binucleophiles (for example, Scheme 3, vii and viii), salts **2** and **3** behave as synthetic equivalents, acting as 1,4-bielectrophiles and forming novel fused five- or six-membered rings.

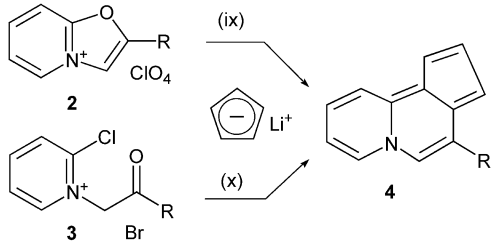


Scheme 3.

However, with some other nucleophiles (e.g. pyridines or KSCN) the salts **2** and **3** either react in different ways[13] or even undergo the concurrent process of pyridine ring opening (as with secondary amines).[14] It was therefore interesting to study the direction and selectivity of reaction of the salts **2** and **3** with CPA. Due to potential 1,2-binucleophilic nature of CPA one would expect (by analogy to Scheme 3) the formation of two C–C bonds [like it is in reaction (vii) with CH_3NO_2] leading to novel six-membered ring [similar to ring expansion (viii) with N_2H_4], thus opening the way to novel pseudoazulene scaffolds by the strategy of Scheme 2.

Results and Discussion

We found that oxazolo[1,2-*a*]pyridinium salts **2** react with lithium cyclopentadienylide in THF at room temperature, leading to previously unknown cyclopenta[*a*]quinolizines **4** (Scheme 4, ix).



Scheme 4.

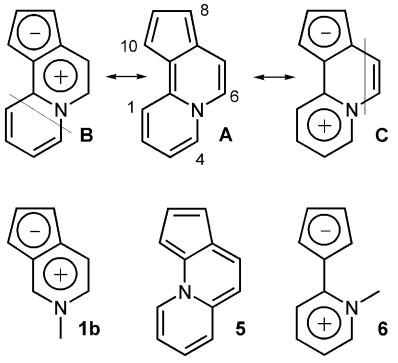
Conversion of **2** into **4** proceeds in moderate yields (35–44% for R = Ar and 13% for R = Me, see Table 1). The same result was observed when salts **2** were changed into monocyclic 2-chloropyridiniums salt **3** (Scheme 4, x), although the yield was lower. Obtained crystalline compounds **4** have deep red color and intense fluorescence; they are stable in air, although they slowly decompose on TLC plates. The constitution of compounds **4** followed from their elementary analysis data and mass spectra, and their structures were confirmed by ^1H and ^{13}C NMR spectroscopy. (Assignment of signals for **4a** was performed by COSY, HMBC, and HSQC experiments.) Finally, the crystal structure of **4a** was determined by X-ray diffraction.

Table 1. Reaction of oxazolo[3,2-*a*]pyridinium **2** and 2-chloro-*N*-phenacylpyridinium **3** salts with lithium cyclopentadienylide.

Entry	Substrate	R	Product	Yield [%]
1	**2a**	4-ClC_6H_5	**4a**	35
2	**2b**	4-MeC_6H_5	**4b**	44
3	**2c**	Me	**4c**	13
4	**3a**	4-ClC_6H_5	**4a**	11

Reactions ix and x (Scheme 4) represent novel examples of combining 1,2-binucleophilic CPA and 1,4-bielectrophilic salts **2** and **3** and look similar to the other reactions outlined in Schemes 2 and 3. On the other hand, conversion of **2** into **4** (oxazole into pyridine) has a parallel to the Kondrat′eva reaction (where oxazoles react as azadienes with alkenes[15]). Meanwhile, from the viewpoint of the pyridine ring synthesis,[16] the observed *polar disconnection* of the central pyridine nucleus of **4** in Scheme 4 belongs to a quite rare combination of synthons $(C^-C^-)+(C^+NCC^+)$. Although some hydrogenated derivatives of **4** have been reported,[17] fully unsaturated skeleton **4** was not known. Up to now, the only reported example of tricyclic pseudoazulene isomeric to **4** is cyclopenta[*c*]quinolizine **5**,[18] which has another type of junction between the carbocycle and quinolizine moieties.

Neutral structure **A** of tricycle **4** can be represented by two nonequivalent dipolar resonance forms **B** and **C** (Scheme 5). The resonance A–B in **4** is similar to that in pyrindine **1b** (X = NR), whereas the resonance A–C is analogous to that in pyridofulvene **6**. As is evident, partial localization of the double bonds in the quinolizine fragment of **4** is expected for all three structures.



Scheme 5.

Experimentally observed bond lengths from our X-ray study (Figure 1) may help to clarify the actual contribution of structures **A**, **B**, and **C**. No bond alternation is observed in the fulvene fragment of **4** and, consequently, the negative charge is delocalized around the five-membered ring. However, the presence of significant double bond character of C6–C7 and a butadiene-like pattern for C1–C2–C3–C4 may indicate that the actual contribution of resonance structures **B** and **C** is equal. Therefore, flat tricycle **4** with a 14 π-

electron system is undoubtedly an aromatic system with significant delocalization of the nitrogen lone pair of electrons toward the fulvene moiety and partial bond localization in the quinolizine part.

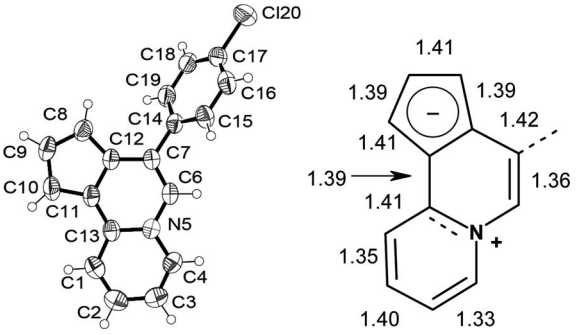
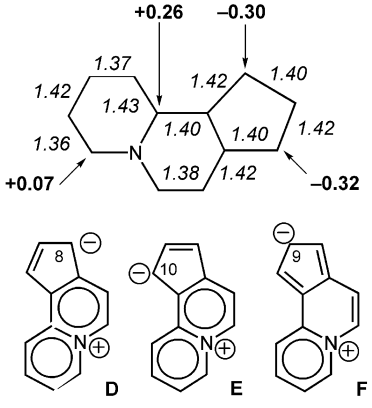


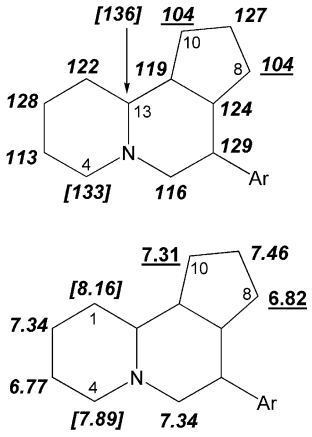
Figure 1. Left: ORTEP drawing for **4a** (with atom numbering scheme). Right: C–C bond lengths [Å] in **4a** according to X-ray data (aryl group is not shown).

The above statement can be confirmed by quantum chemical analysis of structure **4a** (ab initio and PM3), where the calculated lengths of the bonds are in reasonable agreement with the experimental values (Scheme 6). Furthermore, in PM3 the overall π-electron population of the cyclopentadienyl fragment is 5.35, thus confirming its π-excessive nature. The negative charge is mainly located at positions 8 and 10, but not at the C9 atom. This can be rationalized by simple observation that in structures **D** and **E** (Scheme 6) the positive charge can be effectively delocalized around *both* pyridine rings, whereas in structure **F** such delocalization involves only *one* (terminal) six-membered cycle with a quinonoid central ring. This charge separation leads to a high dipole moment (the calculated μ value is 5.25 D for **4a**).



Scheme 6. Calculated bond lengths [Å] in **4a** with highest and lowest natural charges and various possibilities of charge (de)localization.

Because the charges in polar aromatic structures are frequently linked to experimentally observed signals in their NMR spectra, it seems didactical to compare the chemical shifts of novel structures **4** with the data for other (pseudo)-azulenes. The most upfield chemical shifts in the ^{13}C NMR spectra of **4** (both at δ = 104 ppm, underlined in Scheme 7) correspond to the most electron rich carbon atoms C8 and C10 in full agreement with structures **D** and **E**. (Interestingly, this value is close to δ = 102 ppm in CPA.) The matching "underlined" atoms in 2*H*-pyridine **1b** have the same shifts (δ = 103 and 105 ppm[19]), whereas in azulene it is 118 ppm for electron-rich atoms C1 and C3.[20a] Hence, pseudoazulenes **1b** and **4** appear to be more π-excessive than the parent azulene. Remarkably, "noncharged" atom C9 in **4** resonates at much lower field (δ = 127 ppm), indicating no contribution of structure **F**; the same trend was observed for atom C2 of azulene (δ = 137 ppm). The most downfield signals in **4** are observed for the C4 and C13 atoms (δ = 133 and 136 ppm). Again, according to ab initio calculations just these atoms (two α-positions to the nitrogen in the terminal pyridine ring) have the highest positive natural charges (see Scheme 6).



Scheme 7. Observed chemical shifts in the ^{13}C (top) and ^{1}H (bottom) NMR spectra of **4a** (δ, ppm). Minimal values are underlined; maximal shifts are shown in square brackets.

^{1}H NMR spectra of **4** display a similar trend. Thus, the positions of most upfield signals H8 and H10 (δ = 6.82 and 7.31 ppm) and strongly downfield signal H4 (δ = 7.89 ppm) are parallel to their ^{13}C chemical shifts as well as to the highest and lowest charges. [In the analogs of **4** the shifts of the corresponding ("underlined") protons in the five-membered fragment are at δ = 6.6–6.9 ppm[19] for pyrindines **1b** and at δ = 7.35 ppm for azulene.[20b]] However, the highest δ value in tricycle **4** is observed for the H1 proton at δ = 8.16 ppm. This effect, being caused by the short distance H1–H10, is not surprising: in many angular tricycles, where a pair of protons from two nonadjacent rings has close proximity, such signals are frequently shifted downfield (like in angular isomer **5**[18] or phenanthrenes[20c]).

Inspection of proton coupling constants is another useful tool to study the conjugation in aromatic systems. According to Hess and Schaad[21] the value $J_{ratio} = J_{ab}/J_{bc}$ (for a triad of protons along a flat aromatic ring) is a good measure of conjugation of adjacent single/double bonds: the higher the value of J_{ratio}, the better the delocalization. The J_{ratio} value for the five-membered ring is 0.75 for structure **4c**, which is close to that of 2*H*-pyridine (0.80) and which

exceeds the J_{ratio} value of fulvene **6** (0.51). For the pyridine fragment, J_{ratio} = 0.74 for **4c** (taken for triad H1–H2–H3), which is slightly higher than that for pyridofulvene **6** and indolizine **1c** (0.71 for both). These data open another (complementary to X-ray results) viewpoint to understand the nature of bond conjugation in pseudoazulenes **4**.

Absorbance of light in the visible region is typical for blue azulene ($\lambda_{max} \approx 700$ nm), and pseudoazulenes **1b** have a yellow to orange color (λ_{max} = 426 nm for X = O[22] and λ_{max} = 432 for X = NMe[19]). The electronic spectra of tricycles **4** display a broad shoulder at 460–570 nm responsible for their red color. The spectra of **4** (Figure 2), which are different from those of **1b** by an additional broad maxima at 350–420 nm, strongly resemble the spectra of pyridofulvene **6** (with red-orange color and two broad maxima at λ = 360–400 and 450–560).[23] Therefore, the color of **4**, similarly to **6**, is probably linked to charge transfer from the five- to six-membered terminal ring (cf. dipolar structure **C** in Scheme 5).

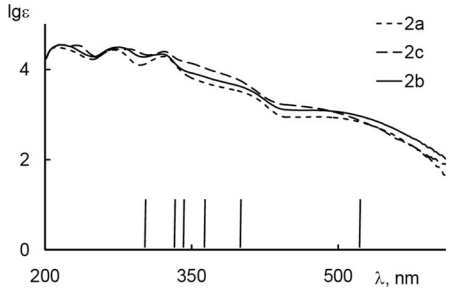


Figure 2. Electronic spectra of **4a**–**c** in ethanol. Vertical lines correspond to calculated values for **4a**.

Because the five-membered ring has a major contribution to the HOMO of **4** and the terminal pyridine ring has a major contribution to its LUMO (Figure 3), it seems reasonable to assign the shoulder appearing at long wavelength in the spectra of **4** to the transition from the HOMO to the LUMO. However, the quantitative picture is not so straightforward, and the calculated HOMO–LUMO gap, as in the case of azulene,[23] does *not* correspond numerically to the observed band that is responsible for the color of **4**. The best theoretical simulation of the experimentally observed UV/Vis spectra of **4** was achieved (see vertical lines in Figure 2) by DFT calculation involving at least six excited states.

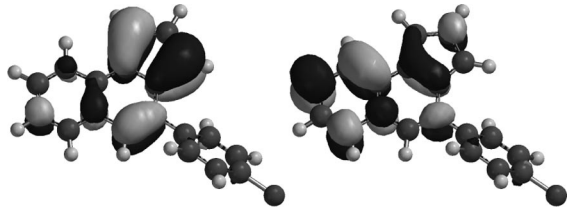


Figure 3. Frontier orbitals of **4a**. Left: HOMO; right: LUMO.

Conclusions

We have expanded the strategy in Scheme 2 and succeeded to prepare novel and more complex pseudoazulene scaffold **4** from salts **2** and **3**. The key step in the conversion of salts **2** to **4** is a previously unknown ring expansion of the oxazolium ring under the action of CPA. This reaction seems to have more general character: according to our preliminary data,[19] other oxazolium salts, fused and monocyclic, may be also involved in such a transformation. The discovered route to tricycles **4** is quite economical, as parent salts **2** and **3** can be prepared easily[12] from cheap materials like α-bromoketones and α-substituted pyridines or pyridones.

As we have proved (X-ray, various spectral methods and calculations), the structure of tricycle **4**, which can be alternatively named *pyrido[1,2-f]2H*-pyrindine, is not just a formal junction of pyridine to 2*H*-pyrindine. Rather, the attached pyridine ring resembles that in pyridofulvene **6** and contains the most π-deficient centers of entire molecule **4**. From the structural viewpoint, tricycle **4** appeared to be a sort of union of three parts, namely, a butadiene fragment of the terminal six-membered ring, significant double bond character of the central ring, and a strongly dipolar aminofulvene residue.

It is important that parent pyrindines **1b** (X = NR) are usually unstable compounds, whereas their pyridoannelated derivatives **4** are quite stable. Therefore, the newly discovered tricycle (isomeric and isostructural to naphthopyrroles or benzoindoles) may serve as an attractively simple scaffold for applications in medicinal chemistry and materials science.

Experimental Section

General Methods: Commercial reagents were used as received, unless otherwise stated. For the synthesis of salts **2** and **3**, see ref.[12] ^{1}H and ^{13}C NMR spectra were recorded with either a Bruker AC-400 or Bruker DRX-500 spectrometer. Chemical shifts were measured by using the δ scale with $SiMe_4$ as the internal standard. LCMS analyses (ES) were performed with a Perkin–Elmer API 150 MCA mass spectrometer. Elemental analyses were obtained with a Karlo Erba 1106 apparatus. UV/Vis spectra were recorded with a Hitachi U-2900 spectrometer. Analytical thin-layer chromatography (TLC) was carried out on "Silufol" silica gel plates (supported on aluminum) by using UV light (254 and 365 nm) for visualization. Experimental intensities of diffraction reflections of single crystal of compound **4a** were measured with a CAD4 automated diffractometer at room temperature;[24] all subsequent calculations were carried out with the SHELX97 program package. Quantum chemical calculations were carried out by using the Spartan 08 package (Wavefunction Inc.); DFT method (B3LYP with 6-31+G* basis set) was used for geometry optimization, calculation of Natural charges, HOMO/LUMO visualization and UV/Vis spectra simulation, whereas π-charges were calculated by PM3 method.

General Procedure for the Preparation of Pyrido[1,2-*f*]2*H*-pyrindines 4 from Salts 2: Cyclopentadienyllithium (554 mg, 7.7 mmol) was added to a suspension of correspondent oxazolo[3,2-*a*]pyridinium salt **2** (6.0 mmol) in absolute THF (60 mL) under an inert atmosphere, and the mixture was stirred for a 48 h at room temperature.

The resulting mixture was evaporated in vacuo and purified by column chromatography on silica (CH_2Cl_2).

7-(4-Chlorophenyl)cyclopenta[*a*]quinolizine (4a): From salt **2a**: 44%, m.p. 141 °C, red solid. R_f = 0.48 ($CHCl_3$/MeOH, 10:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.77 (m, 1 H, H3), 6.82 (d, J = 2.0 Hz, 1 H, H8), 7.31 (d, J = 3.5 Hz, 1 H, H10), 7.34 (s + m, 2 H, H2 + H6), 7.46 (m, 1 H, H9), 7.52 (m, 2 H, ArH, AA′), 7.76 (m, 2 H, ArH, BB′), 7.89 (d, J = 7.0 Hz, 1 H, H4), 8.16 (d, J = 9.0 Hz, 1 H, H1) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 103.6 (C10), 103.8 (C8), 113.3 (C3), 115.9 (C6), 119.0 (C11), 122.1 (C1), 123.8 (C12), 127.2 (C9), 128.4 (C2), 128.7 (Ar), 128.8 (Ar + C7), 132.9 (C4), 133.93 (Ar), 135.9 (C13), 136.3 (Ar) ppm. MS (ES): m/z = 278 [M + H]$^+$. UV (C_2H_5OH): λ (log ε) = 213 (4.49), 271 (4.43), 329 (4.49) nm. $C_{18}H_{12}ClN$ (277.76): calcd. C 77.84, H 4.35, N 5.04; found C 77.63, H 4.55, N 4.94.

7-(4-Methylphenyl)cyclopenta[*a*]quinolizine (4b): From salt **2b**: 56%, m.p. 66 °C, red solid. R_f = 0.33 ($CHCl_3$/MeOH, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3 H, CH_3), 6.75 (m, 1 H), 6.88 (dd, J = 1.3, 3.3 Hz, 1 H), 7.32 (m, 2 H), 7.39 (m, 2 H, ArH, AA′), 7.42 (s, 1 H), 7.45 (m, 1 H), 7.78 (m, 2 H, ArH, BB′), 7.90 (d, J = 7.0 Hz, 1 H), 8.16 (d, J = 9.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 103.4, 104.1, 113.4, 116.1, 119.1, 122.2, 124.5, 127.1, 128.4, 128.7, 129.5, 131.3, 133.1, 135.1, 136.0, 138.1 ppm. MS (ES): m/z = 258 [M + H]$^+$. UV (C_2H_5OH): λ (log ε) 217 (4.51), 276 (4.46), 321 (4.30) nm. $C_{19}H_{15}N$ (257.34): calcd. C 88.68, H 5.88, N 5.44; found C 88.63, H 5.92, N 5.45.

7-Methylcyclopenta[*a*]quinolizine (4c): From salt **2c**: 18%, m.p. 93 °C, red solid. R_f = 0.29 ($CHCl_3$/MeOH, 10:1). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 2.50 (s, 3 H, CH_3), 6.52 (dd, J = 1.5, 3.0 Hz, 1 H), 6.88 (m, 1 H), 7.06 (dd, J = 1.5, 4.0 Hz, 1 H), 7.09 (m, 1 H), 7.41 (ddd, J = 1.3, 6.7, 9.0 Hz, 1 H), 7.59 (s, 1 H), 8.13 (d, J = 8.3 Hz, 1 H), 8.34 (d, J = 6.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8, 102.3, 103.0, 113.1, 116.4, 118.1, 122.2, 126.1, 126.4, 126.9, 128.1, 132.7, 136.1 ppm. MS (ES): m/z = 182 [M + H]$^+$. UV (C_2H_5OH): λ (log ε) 217 (4.51), 276 (4.46), 321 (4.30) nm. $C_{13}H_{11}N$ (181.24): calcd. C 86.15, H 6.12, N 7.73; found C 86.48, H 6.16, N 7.35.

Reaction of Cyclopentadienyllithium with Pyridinium Salt 3a: Cyclopentadienyllithium (1.1 g, 12.0 mmol) was added to a suspension of 2-chloro-1-[2-(4-chlorophenyl)-2-oxoethyl]pyridinium bromide (2.09 g, 6.0 mmol) in absolute THF (60 mL) under an inert atmosphere, and the mixture was stirred for 48 h at room temperature. The resulting mixture was evaporated in vacuo and purified by column chromatography on silica (CH_2Cl_2). 7-(4-Chlorophenyl)cyclopentaquinolizine (**4a**) was obtained in 11% yield.

CCDC-777136 (for **4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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