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INTRAMOLECULAR FREE-RADICAL SUBSTITUTION OF PYRIDINIUM RINGS.

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Abstract. Intramolecular free radical substitution of pyridinium salts has been accomplished giving good yields of [6,5]-, [6,6]- and [6,7]- bicyclic compounds.

The chemistry of pyridines has been extensively investigated for well over one hundred years and some excellent reviews on the subject are available[1]. The free radical substitution chemistry of protonated pyridines is more recent but has still been the subject of extensive research, most notably by Minisci's group[2]. In recent years this chemistry has begun to be used by many groups [3]. However, there are notable gaps in the applications. Prime among these was the absence of intramolecular examples of the substitution reaction[4]. Since many important bicyclic systems would arise by reducing fused pyridinium compounds, we decided to investigate whether intramolecular substitution of N-alkylpyridinium salts could be observed. Although substituted pyridinium compounds are available by other methods e.g. Shono's reaction[5], the directness of the method through intramolecular free-radical substitution makes this approach extremely attractive. This paper[6] reports the efficient formation of [6,5]-, [6,6]- and [6,7]- bicyclic systems under defined conditions.

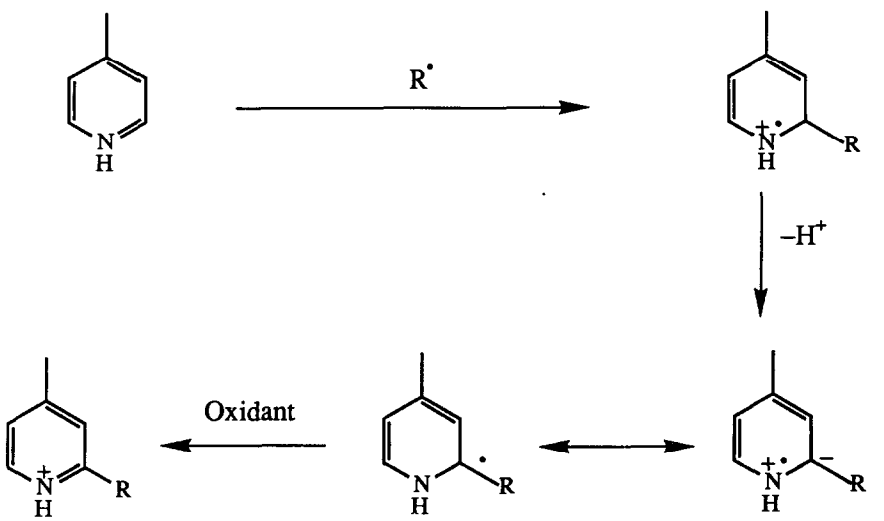


Figure 1

The conditions used by Minisci for intermolecular substitution are all oxidative. As shown in figure 1, the oxidative conditions are useful in regenerating the final aromaticity of the product. Our chemistry[7] has focused principally on the development of methods using reductive conditions since the radicals involved in these chemistries (e.g. thiyl or trialkylstannyl) tend to be less aggressive in their reactions than the oxidative ones (such as alkoxyl or aminyl). The problem with using trialkyltin radicals

generated from trialkyltin hydride would be that these should not generate an aromatic product but rather a dihydropyridine. The ultimate success of this study would then be dependent on the ease of oxidation of these compounds to pyridinium salts.

The first substrate was easily generated by alkylating pyridine with 1,4-diiodobutane. This generated a mixture of the desired monosalt (1) and the disalt (2). Chromatographic separation followed by reaction with tributyltin hydride and the radical initiator AIBN, led initially to very disappointing results until we discovered that the reaction proceeded much better in the presence of large amounts of AIBN. Using this knowledge led to efficient formation of the tetrahydroquinolizinium salt (3). The crude n.m.r. spectrum obtained after evaporation of solvent showed in the downfield region (δ>5) solely the peaks due to the desired pyridinium salt. No signals due to a dihydropyridine were seen; it was assumed that the intermediate dihydropyridine is easily oxidised on exposure to air. Separate n.m.r. studies which we have performed indicate that these compounds do indeed oxidise very rapidly.

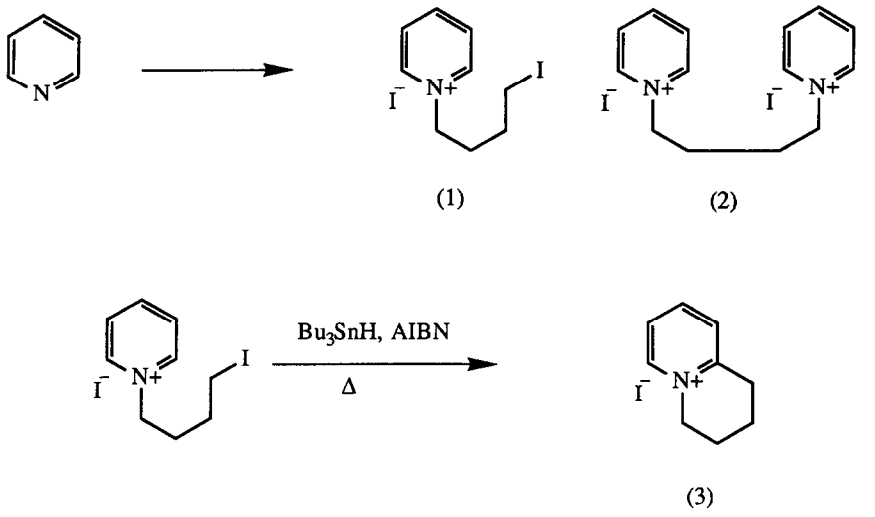
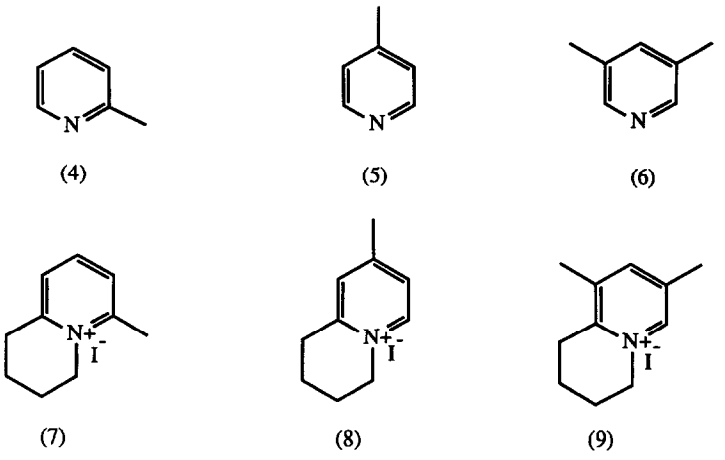


Figure 2

For this reaction to be useful would require that the presence of substituents should not affect the radical chemistry. By starting with the iodobutyl salts derived from the substituted pyridines (4), (5) and (6) pyridines analogous reactions led to the desired products (7),(8) and (9) cleanly, confirming that these substitution patterns were fully compatible with the reaction. Interestingly the substitution of the 2-methylpyridine derivative was regiospecific; no product was detected from addition of the initially formed carbon radical to the 2-position of the pyridinium salt, and the yield of bicyclic product was of the same order as for the other cases. However, when N-iodobutyl-2,6-dimethylpyridinium iodide was used, no product was isolated but the starting material was consumed. This is consistent with the addition of the radical to the pyridinium salt , but the resulting species being unable to progress further towards an aromatic product, and hence forming a reactive dihydropyridine which decomposed during reaction or on attempted isolation. When 3-methylpyridine was used, this gave rise to what appeared from n.m.r. to be a mixture of the two possible aromatic products, but these were not separable in our hands.



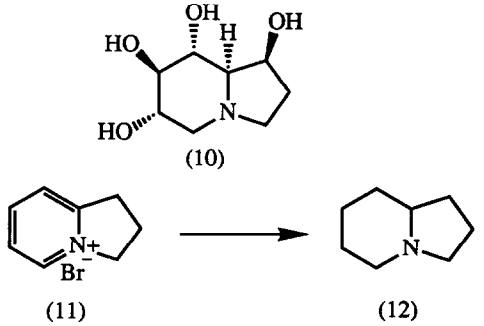
(4) (5) (6)

(7) (8) (9)

Product	Yield
(7)	58%
(8)	58%
(9)	67%

Figure 3

Our interest in these reactions was intensified by the possibility that systems other than [6,6]-bicyclic products could be obtained. In particular, the possibility of generating [6,5]-fused systems was exciting because many saturated [6,5]-fused compounds are glycosidase inhibitors of such prominent interest as anti-viral drugs, e.g. castanospermine (10), and it is known that the [6,5] fused product (11), for example, can be hydrogenated to the saturated indolizidine (12)[8]. We were slightly worried by the possibility of kinetic problems with such cyclisations since they can either be formally viewed as either 5-*endo*- or 5-*exo-trigonal* reactions.



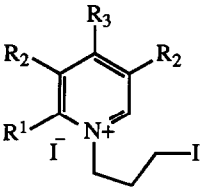
(10)

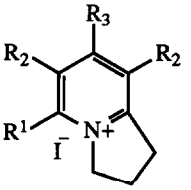
(11) (12)

Figure 4

The cyclisations however proceeded to give good yields of (17) and (18). The compounds (19) and (20) were produced efficiently also but these two products were contaminated with minor amounts of the

corresponding N-propylpyridinium salts, the products of reductive deiodination.

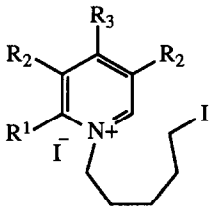


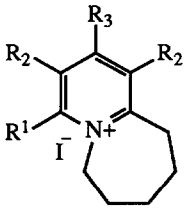


(13) R^1,R^2,R^3=H
(14) R^1=Me, R^2,R^3=H
(15) R^1,R^2=H, R^3=Me
(16) R^1,R^3=H, R^2=Me

(17) R^1,R^2,R^3 =H 65%
(18) R^1=Me, R^2,R^3=H, 65%
(19) R^1,R^2 =H, R^3=Me
(20) R^1,R^3=H, R^2=Me,

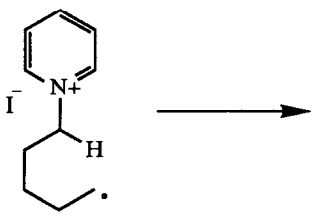
Figure 5





(21) R^1,R^2,R^3=H
(22) R^1=Me, R^2,R^3=H
(23) R^1,R^2=H, R^3=Me
(24) R^1,R^3=H, R^2=Me

(25) R^1,R^2,R^3 =H 58%
(26) R^1=Me, R^2,R^3=H, 58%
(27) R^1,R^2 =H, R^3=Me 79%
(28) R^1,R^3=H, R^2=Me, 66%



(29) (30) (31)

Figure 6

To further extend the scope of the reaction we investigated whether [6,7]- fused rings could form. Here a different potential problem presents itself, in that hydrogen transfer can occur to the primary radical (29) initially generated from the hydrogens on the benzylic carbon so as to give (30). There is literature precedent

for this process when a simple phenyl ring as opposed to a pyridinium ring is present[9]. However, the process is not sufficiently rapid to interfere with the desired reaction in our cases as is seen from figure 6 i.e. [6,7]- compounds were equally efficiently synthesised.

We have investigated whether macrocyclisation[10] would be achievable by attempting cyclisation on the compound (31); this would of course from literature precedent be a very difficult ring size to form. Not surprisingly, this led to reductive de-iodination giving 1-decylpyridinium iodide.

In summary, we have demonstrated that the synthesis of fused pyridinium salts is possible by intramolecular free radical cyclisation. We are currently investigating both the detailed mechanism of the reaction and its scope in synthesis.

Acknowledgments.

We thank the S.E.R.C. for the award of a Quota studentship.

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Experimental Section

Melting points were carried out on a Kofler hot stage apparatus and are uncorrected. Microanalyses were determined using a Perkin-Elmer 240B elemental analyser. Infrared spectra were obtained on a Perkin Elmer 1720-X FTIR or a Pye-Unicam SP3-100 spectrometer. Ultraviolet spectra were recorded on a Philips PU8700 series instrument. ^{1}H n.m.r. spectra were recorded at 90MHz on a Perkin-Elmer R32, at 250MHz on a Bruker WM250 or at 400MHz on a Bruker AM400 machine. ^{13}C n.m.r. spectra were recorded at 23MHz on a Jeol FX90Q, or at 100MHz on a Bruker AM400 machine. N.m.r. experiments were carried out in deuterochloroform, d_4-methanol, d_6-dimethyl sulphoxide or d_3-acetonitrile with tetramethylsilane as internal reference and chemical shifts are quoted in parts per million (δ p.p.m.). The following abbreviations are used s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. In the case of ring systems, assignments are made according to the designated numbering system. Mass spectra were recorded on a VG Micromass 70E or an AEI MS902 instrument. Tetrahydrofuran was distilled from sodium-benzophenone. Acetonitrile was distilled from phosphorus (V) oxide. Pyridine was distilled from calcium hydride. Dichloromethane was distilled from calcium chloride. Diethyl ether, toluene and benzene were dried over sodium wire. Chromatography was performed using Sorbsil C60 (May and Baker), Fluka ACT, Kieselgel HF254 or Kieselgel 60 (Art 9385) silica gels.

General Procedure for the Preparation of 1-(Iodoalkyl)pyridinium Iodides.

The heteroaromatic base (10 mmol) and the diiodoalkane (40 mmol) were refluxed with stirring in acetonitrile (20ml) until t.l.c. showed complete consumption of the heteroaromatic base. The acetonitrile was removed *in vacuo* and the residue was rinsed with ethyl acetate (3 x 10ml) to remove the excess diiodoalkane. The resulting solid was chromatographed on silica with methanol-ethyl acetate (1:1) elution to obtain the partially pure monosalt. Recrystallisation afforded the purified product.

***1-(4-Iodobutyl)pyridinium iodide* (1)**

Obtained as a light yellow crystalline solid from *iso*propanol (77% based on pyridine; m.p. 110°C) (Found : C, 27.90; H, 3.36; N, 3.77; I, 65.39%. $C_9H_{13}NI_2$ requires C, 27.79; H, 3.37; N, 3.60; I, 65.24%); υ_{max} (KBr disc) 3 047, 2 935, 1 635 and 1 486 cm^{-1}; λ_{max} (EtOH) 218 nm (ε 27 100) and 260 (8 300); δ_H (250MHz; CD_3OD) 1.86-1.98 (2H, m, $CH_2CH_2CH_2$), 2.10-2.23 (2H, m, $CH_2CH_2CH_2$) 3.31 (2H, t, *J* 6.8Hz, CH_2CH_2I), 4.73 (2H, t, *J* 7.5Hz, $CH_2CH_2N^+$), 8.16 (2H, m, C3-*H* and C5-*H* (ring)), 8.63 (1H, m, C4-*H* (ring)) and 9.09 (2H, d, *J* 5.5Hz, C2-*H* and C6-*H* (ring)); δ_C (100MHz; CD_3OD) 4.8, 31.1, 33.4, 61.9, 129.6, 146.0 and 147.1; *m/z* (F.A.B., +ve ion; MNBA) 651 ([2*M*-I]$^+$, 14%) and 262 ([*M*-I]$^+$, 100).

1-(4-Iodobutyl) 2-methylpyridinium iodide

Obtained as white plates from *iso*propanol-methanol (64% based on 2-methylpyridine; m.p. 143°C) (Found: C, 29.82; H, 3.74; N, 3.46%. $C_{10}H_{15}NI_2$ requires C, 29.80, H, 3.75, N, 3.48%); υ_{max} (KBr disc) 3 038, 2 939, 1 628, 1 574 and 1 510 cm^{-1}; λ_{max} (EtOH) 218 nm (ε 19 100) and 267 (7 200); δ_H (400MHz; CD_3OD) 1.96-2.13 (4H, m, $CH_2CH_2CH_2CH_2$), 2.93 (3H, s, ArCH_3), 3.33 (2H, t, *J* 6.6Hz, CH_2CH_2I), 4.65 (2H, t, *J* 7.8Hz, $CH_2CH_2N^+$), 7.94 (1H, m, C5-*H* (ring)), 8.02 (1H, d, *J* 7.9Hz, C3-*H* (ring)), 8.45 (1H, m, C4-*H* (ring)) and 8.95 (1H, d, *J* 6.3Hz, C6-*H* (ring)); δ_C (100MHz; CD_3OD) 5.0, 20.6, 31.2, 32.1, 58.2, 127.1, 131.7, 146.6 and 156; *m/z* (F.A.B., +ve ion; MNBA) 679 ([2*M*-I]$^+$, 6%) and 276 ([*M*-I]$^+$, 100).

1-(4-Iodobutyl) 4-methylpyridinium iodide

Obtained as a cream solid from *iso*propanol-methanol (68% based on 4-methylpyridine; m.p. 124-125°C) (Found: C, 29.83; H, 3.76; N, 3.74%. $C_{10}H_{15}NI_2$ requires C, 29.80; H, 3.75; N, 3.48%); υ_{max} (KBr disc) 3 024, 2 936, 1 641, 1 570 and 1 518 cm^{-1}; λ_{max} (EtOH) 220 nm (ε 25 800) and 256 (6 300); δ_H (400MHz; CD_3OD) 1.87-1.94 (2H, m, $CH_2CH_2CH_2$), 2.07-2.17 (2H, m, $CH_2CH_2CH_2$), 2.69 (3H, s, $ArCH_3$), 3.30 (2H, t, *J* 6.8Hz, CH_2CH_2I), 4.65 (2H, t, *J* 7.5Hz, $CH_2CH_2N^+$), 7.96 (2H, d, *J* 6.4Hz, C3-*H* and C5-*H* (ring)) and 8.88 (2H, d, *J* 6.7Hz, C2-*H* and C6-*H* (ring)); δ_C (100MHz; CD_3OD) 4.9, 22.1, 31.1, 33.3, 60.9, 130.0, 144.9 and 161.4; *m/z* (F.A.B. +ve ion; MNBA) 679 ($[2M\text{-}I]^+$, 18%) and 276 ($[M\text{-}I]^+$, 100).

1-(4-Iodobutyl) 3-methylpyridinium iodide

Obtained as a white powder from ethyl acetate-methanol (63% based on 3-methylpyridine; m.p. 80-81°C) (Found: C, 29.75; H, 3.76: N, 3.46%. $C_{10}H_{15}NI_2$ requires C, 29.80; H, 3.75; N, 3.48%); υ_{max} (KBr disc) 3 012, 2 937, 1 633 and 1 507 cm^{-1}; λ_{max} (EtOH) 220 nm (ε 17 000) and 266 (5 000); δ_H (400MHz; CD_3OD) 1.92 (2H, m, *J* 7.3 Hz, $CH_2CH_2CH_2$), 2.17 (2H, m, *J* 7.6Hz, $CH_2CH_2CH_2$), 2.61 (3H, s, $ArCH_3$), 3.31 (2H, t, *J* 6.8Hz, CH_2CH_2I), 4.68 (2H, t, *J* 7.5Hz, $CH_2CH_2N^+$), 8.02 (1H, m, C5-*H* (ring)), 8.45 (1H, d, *J* 8.0Hz, C4-*H* (ring)), 8.88 (1H, d, *J* 6.1Hz, C6-*H* (ring)) and 8.98 (1H, s, C2-*H* (ring)); δ_C (100MHz; CD_3OD) 5.3, 18.9, 31.4, 33.6, 61.9, 129.1, 141.6, 143.3, 145.8 and 147.8; *m/z* (F.A.B., +ve ion; MNBA) 679 ($[2M\text{-}I]^+$, 28%) and 276 ($[M\text{-}I]^+$, 100).

1-(4-Iodobutyl) 3,5-dimethylpyridinium iodide

Obtained as white plates from ethanol (65% based on 3,5-dimethylpyridine; m.p. 177-178°C) (Found: C, 31.57; H, 4.11; N, 3.28%. $C_{11}H_{17}NI_2$ requires C, 31.68; H, 4.11; N, 3.36%); υ_{max} (KBr disc) 3 031, 2 941, 1 631 and 1 495cm^{-1}; λ_{max} (EtOH) 219 nm (ε 21 000) and 272 (6 600); δ_H (400MHz; CD_3OD) 1.86-1.94 (2H, m, $CH_2CH_2CH_2$), 2.09-2.17 (2H, m, $CH_2CH_2CH_2$), 2.54 (6H, s, $ArCH_3$), 3.29 (2H, t, *J* 6.9Hz, CH_2CH_2I), 4.59 (2H, t, *J* 7.5Hz, $CH_2CH_2N^+$), 8.27 (1H, s, C4-*H* (ring)) and 8.74 (2H, s, C2-*H* and C6-*H* (ring)); δ_C (100MHz; CD_3OD) 4.8, 18.4, 31.1, 33.3, 61.5, 140.6, 142.8 and 148.0; *m/z* (F.A.B., +ve ion; MNBA) 706 ($[2M\text{-}HI]^+$, 37%) and 290 ($[M\text{-}I]^+$, 100).

1-(4-Iodobutyl) 2,6-dimethylpyridinium iodide

Obtained as yellow needles from *iso*propanol-methanol (17% based on 2,6-dimethylpyridine; m.p. 184-186°C) (Found: C, 31.80; H, 4.32; N, 3.24; I, 60.64%. $C_{11}H_{17}NI_2$ requires C, 31.68; H, 4.11; N, 3.36; I, 60.86%); υ_{max} (KBr disc) 3 030, 2 943, 2 899, 1 622 and 1 490 cm^{-1}; λ_{max} (EtOH) 219nm (ε 17 000) and 274 (7 900); δ_H (400MHz; d_6-DMSO) 1.89 (2H, m, $CH_2CH_2CH_2$), 2.00 (2H, m, $CH_2CH_2CH_2$), 3.38 (2H, t, *J* 6.9Hz, CH_2CH_2I), 4.51 (2H, t, *J* 8.5Hz, $CH_2CH_2N^+$) 7.90 (2H, d, *J* 7.9Hz, C3-*H* and C5-*H* (ring)) and 8.34 (1H, t, *J* 7.9Hz, C4-*H* (ring)); δ_C (100MHz; d_6-DMSO) 11.2, 24.7, 32.3, 34.0, 55.4, 131.8, 148.3 and 159.5; *m/z* (F.A.B., +ve ion; MNBA) 707 ($[2M\text{-}I]^+$, 15%) and 290 ($[M\text{-}I]^+$, 100).

***1-(3-Iodopropyl)pyridinium iodide* (13)**

Obtained as white crystals from methanol (66% based on pyridine; m.p. 157-158°C) (Found: C, 25.55; H, 2.91; N, 3.82; I, 67.83%. $C_8H_{11}NI_2$ requires C, 25.62; H, 2.96; N, 3.74; I, 67.68%); υ_{max} (KBr disc) 3 039, 3 018, 1 634 and 1 485 cm^{-1}; λ_{max} (EtOH) 218 nm (ε 18 100) and 260 (5 400); δ_H (250MHz; CD_3OD) 2.58 (2H, quintet, *J* 7.1Hz, $N^+CH_2CH_2CH_2I$), 3.29 (2H, t, *J* 6.9Hz, CH_2CH_2I), 4.79 (2H, t,

J 7.3Hz, $CH_2CH_2N^+$), 8.16 (2H, m), 8.64 (1H, m, C4-*H* (ring)) and 9.08 (2H, d, *J* 6.4Hz, C2-*H* and C6-*H* (ring)); δ_C (100MHz; CD_3OD) -0.7, 35.6, 63.3, 129.7, 146.3 and 147.3; *m/z* (F.A.B., +ve ion; MNBA) 623 ([2*M*-I]$^+$, 4%) and 248 ([*M*-I]$^+$, 100).

***1-(3-Iodopropyl) 2-methylpyridinium iodide* (14)**

Obtained as white crystals from ethanol (64% based on 2-methylpyridine; m.p. 126-127°C) (Found: C, 27.75; H, 3.36; N, 3.48%. $C_9H_{13}NI_2$ requires C, 27.79; H, 3.37, N, 3.60%); υ_{max} (KBr disc) 2 991, 1 634, 1 581 and 1 520 cm^{-1}; λ_{max} (EtOH) 218 nm (ε 18 300) and 267 (6 800); δ_H (250MHz; CD_3OD), 2.50 (2H, quintet, *J* 7.0Hz, $^+NCH_2CH_2CH_2I$), 2.95 (3H, s, $ArCH_3$), 3.39 (2H, t, *J* 6.7Hz, CH_2CH_2I), 4.73 (2H, t, *J* 7.8Hz, $CH_2CH_2N^+$), 7.95 (1H, m, C5-*H* (ring)), 8.03 (1H, d, *J* 7.8Hz, C3-*H* (ring)), 8.47 (1H, m, C4-*H* (ring)) and 8.97 (1H, d, *J* 6.2Hz, C6-*H* (ring)); δ_C (100MHz; CD_3OD) 0.0, 20.7, 34.4, 59.7, 127.2, 131.8, 146.7, 146.8 and 157.2; *m/z* (F.A.B., +ve ion; MNBA) 651 ([2*M*-I]$^+$, 7%) and 262 ([*M*-I]$^+$, 100).

***1-(3-Iodopropyl) 4-methylpyridinium iodide* (15)**

Obtained as white plates from ethanol (68% based on 4-methylpyridine; m.p. 137-138°C) (Found: C, 27.81; H, 3.35; N, 3.56%. $C_9H_{13}NI_2$ requires C, 27.79; H, 3.37; N, 3.60%); υ_{max} (KBr disc) 3 016, 1 641 and 1 516 cm^{-1}; λ_{max} (EtOH) 220 nm (ε 20 900) and 257 (4 800); δ_H (250MHz; CD_3OD) 2.54 (2H, quintet, *J* 7.0Hz, $^+NCH_2CH_2CH_2I$), 2.69 (3H, s, $ArCH_3$), 3.27 (2H, t, *J* 6.9Hz, CH_2CH_2I), 4.70 (2H, t, *J* 7.2Hz, $CH_2CH_2N^+$), 7.96 (2H, d, *J* 6.4Hz, C3-*H* and C5-*H* (ring)) and 8.87 (2H, d, *J* 6.8Hz, C2-*H* and C6-*H*(ring)); δ_C (100MHz; CD_3OD) -0.4, 22.2, 35.5, 62.3, 130.1, 145.1 and 161.7; *m/z* (F.A.B, +ve ion; MNBA) 650 ([2*M*-HI]$^+$, 12%) and 262 ([*M*-I]$^+$, 100).

***1-(3-Iodopropyl) 3,5-dimethylpyridinium iodide* (16)**

Obtained as a light yellow powder from ethanol (68% based on 3,5-dimethylpyridine; m.p. 129-130°C) (Found: C, 29.74; H, 3.75; N, 3.39%. $C_{10}H_{15}NI_2$ requires C, 29.80; H, 3.75; N, 3.48%); υ_{max} (KBr disc) 2 999, 2 922, 1 629 and 1 499 cm^{-1}; λ_{max} (EtOH) 219 nm (ε 20 200) and 273 (6 100); δ_H (250MHz; CD_3OD) 2.55 (6H, s, 2 x $ArCH_3$), 2.55 (2H, quintet, *J* 7.0Hz, $^+NCH_2CH_2CH_2I$), 3.28 (2H, t, *J* 6.9Hz, CH_2CH_2I), 4.67 (2H, t, *J* 7.3Hz, $CH_2CH_2N^+$), 8.29 (1H, s, C4-*H* (ring)) and 8.76 (2H, s, C2-*H* and C6-*H* (ring)); δ_C (23MHz; CD_3OD) 0.7, 18.9, 35.8, 62.9, 140.6, 143.0 and 148.5; *m/z* (F.A.B., +ve ion; MNBA) 678 ([2*M*-HI]$^+$, 10%) and 276 ([*M*-I]$^+$, 100).

***1-(5-Iodopentyl)pyridinium iodide* (21)**

Obtained as yellow crystals from ethanol (70% based on pyridine; m.p. 82°C) (Found: C, 29.80; H, 3.74; N, 3.48%. $C_{10}H_{15}NI_2$ requires C, 29.80; H, 3.75; N, 3.47); υ_{max} (KBr disc) 3 038, 2 941, 2 926, 2 852, 1 632 and 1 483cm^{-1}; λ_{max} (EtOH) 218 nm (ε 21 800) and 260 (6 200); δ_H (250MHz; CD_3OD) 1.46-1.58 (2H, m, $CH_2CH_2CH_2$), 1.84-1.96 (2H, m, $CH_2CH_2CH_2$), 2.02-2.15 (2H, m, $CH_2CH_2CH_2$), 3.27 (2H, t, *J* 6.9Hz, CH_2CH_2I), 4.70 (2H, t, *J* 7.6Hz, $CH_2CH_2N^+$), 8.15 (2H, m, C3-*H* and C5-*H* (ring)), 8.63 (1H, m, C4-*H* (ring)) and 9.09 (2H, dd, *J* 5.4, 1.2Hz, C2-*H* and C6-*H* (ring)); δ_C (23MHz; CD_3OD) 7.2, 28.1, 31.4, 34.0, 62.9, 129.7, 146.2 and 147.1; *m/z* (F.A.B., +ve ion; MNBA) 679 ([2*M*-I]$^+$, 10%) and 276 ([*M*-I]$^+$, 100).

***1-(5-Iodopentyl) 2-methylpyridinium iodide* (22)**

Obtained as white crystals from ethanol (68% based on 2-methylpyridine; m.p. 140-141°C) (Found: C, 31.74; H, 4.13; N, 3 27%. $C_{11}H_{17}NI_2$ requires C, 31.68; H, 4.11; N, 3.36%); υ_{max} (KBr disc) 3 054, 3 033,

2 929, 1 631, 1 573, 1 509 and 1 481cm^{-1}; λ_{max} (EtOH) 218 nm (ε 20 300) and 267 (7 600); δ_H (250MHz; CD_3OD) 1.53-1.65 (2H, m, $CH_2CH_2CH_2$), 1.86-2.06 (4H, m, $CH_2CH_2CH_2CH_2$), 2.92 (3H, s, $ArCH_3$), 3.28 (2H, t, *J* 6.8Hz, CH_2CH_2I), 4.62 (2H, t, *J* 7.9Hz, $CH_2CH_2N^+$), 7.93 (1H, m, C5-*H* (ring)), 8.01 (1H, d, *J* 7.9Hz, C3-*H* (ring)), 8.44 (1H,m , C4-*H* (ring)) and 8.94 (1H, dd, *J* 6.2, 1.2Hz, C6-*H* (ring)); δ_C (100MHz; CD_3OD) 6.4, 20.6, 28.2, 30.0, 33.9, 59.1, 127.0, 131.6, 146.5 and 157; *m/z* (F.A.B., +ve ion; MNBA) 706 ([2*M*-HI]$^+$, 12%) and 290 ([*M*-I]$^+$, 100).

***1-(5-Iodopentyl) 4-methylpyridinium iodide* (23)**

Obtained as white needles from ethanol (73% based on 4-methylpyridine; m.p. 114-115°C) (Found: C, 31.72; H, 4.15; N, 3.37%. $C_{11}H_{17}NI_2$ requires C, 31.68; H, 4.11; N, 3.36%); υ_{max} (KBr disc) 3 015, 2 930, 1 642 and 1 520cm^{-1}; λ_{max} (EtOH) 221 nm (ε 29 500) and 256 (6 400); δ_H (250MHz; CD_3OD) 1.44-1.56 (2H, m, $CH_2CH_2CH_2$), 1.83-1.94 (2H, m, $CH_2CH_2CH_2$), 1.98-2.11 (2H, m, $CH_2CH_2CH_2$), 2.69 (3H, s, $ArCH_3$), 3.26 (2H, t, *J* 6.8Hz, CH_2CH_2I), 4.61 (2H, t, *J* 7.5Hz, $CH_2CH_2N^+$), 7.95 (2H, d, *J* 6.4Hz, C3-*H* and C5-*H* (ring)) and 8.87 (2H, d, *J* 6.7Hz, C2-*H* and C6-*H* (ring)); δ_C (23MHz; CD_3OD), 7.3, 22.6, 28.0, 31.2, 34.0, 61.9, 130.1, 145.0 and 161.2; *m/z* (F.A.B., +ve ion; MNBA) 706 ([2*M*-HI]$^+$, 7%) and 290 ([*M*-I]$^+$, 100).

***1-(5-Iodopentyl) 3,5-dimethylpyridinium iodide* (24)**

Obtained as yellow crystals from ethanol (72% based on 3,5-dimethylpyridine; m.p. 100-102°C) (Found: C, 33.31; H, 4.52; N, 3.21%. $C_{12}H_{19}NI_2$ requires C, 33.43; H, 4.44; N, 3.25%); υ_{max} (KBr disc) 3 073, 3 005, 2 939, 2 863, 1 637 and 1 499cm^{-1}; λ_{max} (EtOH) 219 nm (ε 18 800) and 272 (5 900); δ_H (250MHz; CD_3OD) 1.45-1.57 (2H, m, $CH_2CH_2CH_2$), 1.84-1.95 (2H, m, $CH_2CH_2CH_2$), 2.02-2.14 (2H, m, $CH_2CH_2CH_2$), 2.56 (6H, s, 2 x $ArCH_3$), 3.27 (2H, t, *J* 6.8Hz, CH_2CH_2I), 4.60 (2H, t, *J* 7.6Hz, $CH_2CH_2N^+$), 8.29 (1H, s, C4-*H* (ring)) and 8.80 (2H, s, C2-*H* and C6-*H* (ring)); δ_C (23MHz; CD_3OD) 7.2, 18.9, 28.1, 31.3, 34.0, 62.5, 140.5, 142.9 and 148.2; *m/z* (F.A.B., +ve ion; MNBA) 734 ([2*M*-HI]$^+$, 4%) and 304 ([*M*-I]$^+$, 100).

***1-(10-Iododecyl)pyridinium iodide* (31)**

Obtained as light yellow plates from ethanol (68% based on pyridine; m.p. 132-133°C). (Found: C, 38.24; H, 5.42; N, 3.12; I, 53.75%. $C_{15}H_{25}NI_2$ requires C, 38.08; H, 5.33; N, 2.96; I, 53.64%); υ_{max} (KBr disc) 3 039, 3 016, 2 925, 2 850, 1 636 and 1 492 cm^{-1}; λ_{max} (EtOH) 219 nm (ε 14 000) and 259 (3 900); δ_H (250MHz; CD_3OD) 1.36 (12H, m, 6 x $CH_2CH_2CH_2$), 1.78 (2H, m, *J* 7.1Hz, $CH_2CH_2CH_2$), 2.04 (2H, m, $CH_2CH_2CH_2$), 3.23 (2H, t, *J* 6.9Hz, CH_2CH_2I), 4.67 (2H, t, *J* 7.6Hz, $CH_2CH_2N^+$), 8.14 (2H, t, *J* 7.1Hz, C3-*H* and C5-*H* (ring)), 8.61 (1H, tt, *J* 7.8, 1.2Hz, C4-*H* (ring)) and 9.06 (2H, d, *J* 5.4Hz, C2-*H* and C6-*H* (ring)); δ_C (23MHz; $CDCl_3$) 7.1, 25.4, 27.8, 28.3, 28.6, 29.8, 31.3, 32.9, 61.5, 128.1, 144.4 and 145.2; *m/z* (F.A.B., +ve ion; MNBA) 819 ([2*M*-I]$^+$, 5%) and 346 ([*M*-I]$^+$, 100).

General Procedure for the Intramolecular Free Radical Substitution of Quaternised Pyridinium Salts.

The 1-(*n*-iodoalkyl) pyridinium iodide (0.25mmol, 1.0eq) was taken up in dry, distilled acetonitrile-tetrahydrofuran (1:1) (50ml; 5mmolar substrate concentration) and the mixture was brought to reflux, with stirring, under nitrogen. A solution of AIBN (0.30mmol [1.2eq] for 5- and 6-ring formation; 0.50mmol [2.0eq] for 7-ring formation) in tetrahydrofuran (1.0ml) was added in one portion, followed immediately by tri-*n*-butyltin hydride (0.33mmol, 1.3eq) in one portion. The reflux was continued out for 3h, then after

cooling, the solvent was removed *in vacuo*. The crude product was partitioned between acetonitrile (25ml) and 60-80° petrol (3 x 15ml) to remove tri-*n*-butyltin residues. The acetonitrile layer was evaporated and the residue was recrystallised from acetonitrile-ethyl acetate, ethanol-ethyl acetate or acetonitrile-ether.

1,2,3,4-Tetrahydroquinolizinium iodide (**3**)

Obtained from 1-(4-iodobutyl)pyridinium iodide (**1**) as a light yellow solid (60%; m.p. 178-182°C) (Found: M^+, 261.0015. $C_9H_{12}NI$ requires *M*, 261.0013); υ_{max} (KBr disc) 3 001, 2 953, 1 632, 1 582 and 1 512cm^{-1}; λ_{max} (EtOH) 217 nm (ε 20 800) and 267 (7 600); δ_H (250MHz; CD_3CN), 2.00-2.11 (2H, m, $CH_2CH_2CH_2$), 2.15-2.25 (2H, m, $CH_2CH_2CH_2$), 3.33 (2H, t, *J* 6.5Hz CH_2CH_2Ar), 4.67 (2H, t, *J* 6.0Hz, $CH_2CH_2N^+$), 7.86 (1H, m, C7-*H*), 7.93 (1H, d, *J* 8.1Hz, C9-*H*), 8.40 (1H, m, C8-*H*) and 8.76 (1H, d, *J* 6.1Hz, C6-*H*); δ_C (100MHz; CD_3OD) 18.6, 22.2, 29.5, 57.1, 126.2, 130.2, 145.6, 145.9 and 158; *m/z* (200°C) 261 (M^+, 1%), 138 (100) and 134 (22).

6-Methyl 1,2,3,4-tetrahydroquinolizinium iodide (**7**)

Obtained from 1-(4-iodobutyl) 2-methylpyridinium iodide as a pink powder (58%; dec. > 190°C) (Found: C, 43.74; H, 5.39; N, 5.19; I, 46.37%. $C_{10}H_{14}NI$ requires C, 43.66; H, 5.13; N, 5.09; I, 46.12%); υ_{max} (KBr disc) 3 040, 3 014, 2 945, 2 873, 1 631, 1 587 and 1 490cm^{-1}; λ_{max} (EtOH) 217 nm (ε 21 200) and 275 (9 000); δ_H (400MHz; CD_3CN) 1.90-1.98 (2H, m, $CH_2CH_2CH_2$), 2.11-2.17 (2H, m, $CH_2CH_2CH_2$), 2.77 (3H, s, $ArCH_3$), 3.25 (2H, t, *J* 6.7Hz, CH_2CH_2Ar), 4.41 (2H, t, *J* 6.2Hz, $CH_2CH_2N^+$), 7.69 and 7.71 (2H, 2 x d, *J* 8Hz, C7-*H* and C9-*H*) and 8.20 (1H, t, *J* 7.9Hz, C8-*H*); δ_C (100MHz; CD_3CN) 17.7, 21.8, 22.1, 30.5, 52.3, 127.6, 127.8, 144.3, 156.1 and 158.1; *m/z* (180°C) 148 (M^+-I, 17%) and 146 (100).

8-Methyl 1,2,3,4-tetrahydroquinolizinium iodide (**8**)

Obtained from 1-(4-iodobutyl) 4-methylpyridinium iodide as a white solid (58%; m.p. 143-146°C) (Found: C, 43.70; H, 5.24; N, 5.24%. $C_{10}H_{14}NI$ requires C, 43.66; H, 5.13; N, 5.09%); υ_{max} (KBr disc) 3 031, 2 997, 2 969, 2 940, 1 638 and 1 573cm^{-1}; λ_{max} (EtOH) 220 nm (ε 20 500) and 264 (5 900); δ_H (250MHz; CD_3OD) 1.97-2.08 (2H, m, $CH_2CH_2CH_2$), 2.12-2.22 (2H, m, $CH_2CH_2CH_2$), 2.60 (3H, s, $ArCH_3$), 3.26 (2H, t, *J* 6.6Hz, CH_2CH_2Ar), 4.59 (2H, t, *J* 6.1Hz, $CH_2CH_2N^+$), 7.69 (1H, d, *J* 6.4Hz, C7-*H*), 7.76 (1H, s, C9-*H*) and 8.57 (1H, d, *J* 6.5Hz, C6-*H*); δ_C (100MHz; CD_3OD), 18.6, 21.8, 22.3, 29.3, 56.3, 127.0, 130.2, 144.9, 156.9 and 159.4; *m/z* (180°C) 148 (M^+-I, 11%) and 146 (100).

7,9-Dimethyl 1,2,3,4-tetrahydroquinolizinium iodide (**9**)

Obtained from 1-(4-iodobutyl) 3,5-dimethylpyridinium iodide as a yellow powder (67%; dec. > 109°C) (Found: M^+-I, 162.1235. $C_{11}H_{16}N$ requires *M*, 162.1283); υ_{max} (KBr disc) 2 993, 2 967, 1 629 and 1 504cm^{-1}; λ_{max} (EtOH) 219 nm (ε 17 900) and 278 (6 500); δ_H (400MHz; CD_3CN) 1.95-2.03 (2H, m, $CH_2CH_2CH_2$), 2.06-2.12 (2H, m, $CH_2CH_2CH_2$), 2.39 (3H, s, $ArCH_3$), 2.42 (3H, s, $ArCH_3$), 3.07 (2H, t, *J* 6.6Hz, CH_2CH_2Ar), 4.56 (2H, t, *J* 5.9Hz, $CH_2CH_2N^+$), 8.07 (1H, s, C8-*H*) and 8.45 (1H, s, C6-*H*); δ_C (100MHz; CD_3CN) 17.8, 18.7, 18.8, 21.6, 26.8, 57.4, 135.7, 138.6, 142.7, 146.6 and 153.6; *m/z* (180°C) 162 (M^+-I, 8%) and 160 (100).

2,3-Dihydro-1H-indolizinium iodide (**17**)[11]

Obtained from 1-(3-iodopropyl)pyridinium iodide (**13**) as a yellow solid (65%; m.p. 106-108°C [lit.[11] m.p. 112-114°C]) (Found: C, 39.07; H, 4.18; N, 5.33%. $C_8H_{10}NI$ requires C, 38.89; H, 4.08; N, 5.67%); υ_{max} (KBr disc) 3 040, 2 938, 1 625 and 1 499cm^{-1}; λ_{max} (EtOH) 218 nm (ε 21 300) and 265 (6 900); δ_H

(400MHz; CD_3CN) 2.48 (2H, quintet, *J* 7.7Hz, $^+NCH_2CH_2CH_2Ar$), 3.52 (2H, t, *J* 7.7Hz, CH_2CH_2Ar), 4.86 (2H, t, *J* 7.7Hz, $CH_2CH_2N^+$), 7.87 (1H, m, C6-*H*), 8.00 (1H, d, *J* 8.0Hz, C8-*H*), 8.41 (1H, m, C7-*H*) and 8.83 (1H, d, *J* 6.1Hz, C5-*H*); δ_C (100MHz; CD_3CN) 22.1, 33.2, 60.2, 125.8, 126.4, 142.0, 146.1 and 160; *m/z* (200°C) 120 (M^+-I, 6%) and 117 (100).

***5-Methyl 2,3-dihydro-1H-indolizinium iodide* (18)**

Obtained from 1-(3-iodopropyl) 2-methylpyridinium iodide (**14**) as a white solid (65%; dec. > 205°C) (Found: C, 41.67; H, 4.75; N, 5.49%. $C_9H_{12}NI$ requires C, 41.40; H, 4.63; N, 5.36%); υ_{max} (KBr disc) 3 019, 2 957, 1 632, 1 588 and 1 494cm^{-1}; λ_{max} (EtOH) 217 nm (ε 23 100) and 271 (9 500); δ_H (400MHz; CD_3CN) 2.45 (2H, quintet, *J* 7.8Hz, $^+NCH_2CH_2CH_2Ar$), 2.75 (3H, s, $ArCH_3$), 3.52 (2H, t, *J* 7.9Hz, CH_2CH_2Ar), 4.71 (2H, t, *J* 7.6Hz, $CH_2CH_2N^+$), 7.71 (1H, d, *J* 7.8Hz, C6-*H*), 7.79 (1H, d, *J* 7.9Hz, C8-*H*) and 8.27 (1H, t, *J* 7.9Hz, C7-*H*), δ_C (100MHz; CD_3CN) 20.8, 21.5, 33.4, 58.1, 122.8, 127.2, 145.7, 154 and 159.9; *m/z* (200°C) 134 (M^+-I, 9%) and 132 (100).

***7-Methyl 2,3-dihydro-1H-indolizinium iodide* (19)**

Obtained from 1-(3-iodopropyl) 4-methylpyridinium iodide (**15**) as a 4:1 mixture with ***1-propyl 4-methylpyridinium iodide*** as a deliquescent light yellow solid (68%; m.p. 85-87°C [sealed tube]) (cyclised material (**19**): Found : M^+–I, 134.0956. $C_9H_{12}N$ requires *M*, 134.0969; uncyclised material : Found : M^+-I, 136.1099. $C_9H_{14}N$ requires *M*, 136.1126); υ_{max} (KBr disc) 3 020, 2 969, 1 640, 1 568 and 1 502cm^{-1}; λ_{max} (EtOH) 218 nm (ε 13 700) and 262 (4 700); δ_H (400MHz; CD_3CN) cyclised material (**19**): 2.46 (2H, quintet, *J* 7.7Hz, $^+NCH_2CH_2CH_2Ar$), 2.60, (3H, s, $ArCH_3$), 3.45 (2H, t, *J* 7.7Hz, CH_2CH_2Ar), 4.78 (2H, t, *J* 7.7Hz, $CH_2CH_2N^+$), 7.68 (1H, d, *J* 6.1Hz, C6-*H*), 7.80 (1H, s, C8-*H*) and 8.66 (1H, d, *J* 6.3Hz, C5-*H*); uncyclised material : 0.95 (3H, t, *J* 7.4Hz, CH_2CH_3), 2.0 (2H, sextet (partly obscured), *J* 7.4Hz, $^+NCH_2CH_2CH_2Ar$), 2.64 (3H, s, $ArCH_3$), 4.54 (2H, t, *J* 7.4Hz, $CH_2CH_2N^+$), 7.88 (2H, d, *J* 6.1Hz, C3-*H* and C5-*H* (ring)) and 8.77 (2H, d, *J* 6.6Hz, C2-*H* and C6-*H* (ring)); δ_C(100MHz; CD_3CN) cyclised material (**19**): 22.3, 22.4, 33.0, 59.5, 126.0, 127.3, 141.0 and 160.0; uncyclised material : 10.6, 25.4, 63.0, 129.7, 144.6 and 161; *m/z* (200°C) cyclised material (**19**): 134 (M^+-I, 7%) and 93 (100); uncyclised material : 136 (M^+-I, 13%).[The 4:1 ratio of cyclised to uncyclised material was improved to 8:1 by using 10 equivalents of AIBN].

***6,8-Dimethyl 2,3-dihydro-1H-indolizinium iodide* (20)**

Obtained from 1-(3-iodopropyl) 3,5-dimethylpyridinium iodide (**16**) as a 17:1 mixture with ***1-propyl 3,5-dimethylpyridinium iodide*** as a white solid (71%; dec. > 128°C) (cyclised material (**20**): Found : M^+-HI, 147.1016. $C_{10}H_{13}N$ requires *M*, 147.1048); υ_{max} (KBr disc) 2 986, 2 952, 1 636 and 1 512cm^{-1}; λ_{max} (EtOH) 218 nm (ε 20 300) and 276 (6 800); δ_H (400MHz; CD_3CN) cyclised material (**20**): 2.43 (3H, s, $ArCH_3$), 2.45 (3H, s, $ArCH_3$), 2.45 (2H, quintet *J* 7.6Hz, $^+NCH_2CH_2CH_2Ar$), 3.39 (2H, t, *J* 7.6Hz, CH_2CH_2Ar), 4.82 (2H, t, *J* 7.8Hz, $CH_2CH_2N^+$), 8.08 (1H, s, C7-*H* (ring)) and 8.57 (1H, s, C5-*H* (ring)); uncyclised material : 0.95 (3H, t, *J* 7.4Hz, CH_2CH_3), 2.01 (2H, sextet, *J* 7.4Hz, $CH_2CH_2CH_3$), 2.50 (6H, s, 2 x $ArCH_3$), 4.52 (2H, t, *J* 7.4Hz, $CH_2CH_2N^+$), 8.20 (1H, s, C4-*H*) and 8.72 (2H, s, C2-*H* and C6-*H*); δ_C (100MHz; CD_3CN) cyclised material (**20**): 17.8, 17.9, 21.3, 31.6, 60.2, 135.5, 136.9, 138.3, 146.7 and 156; *m/z* (200°C) cyclised material : 147 (M^+-HI, 11%) and 145 (100).

***7,8,9,10-Tetrahydro-6H-pyrido[1,2-a]azepinium iodide* (25)**

Obtained from 1-(5-iodopentyl)pyridinium iodide (**21**) as a light yellow solid (58%; dec. > 95°C) (Found: M^+-I, 148.1106. $C_{10}H_{14}N$ requires M, 148.1126); υ_{max} (KBr disc) 3 005, 2 929, 2 855, 1 627, 1 579 and 1 520cm^{-1}; λ_{max} (EtOH) 218 nm (ε 22 500) and 268 (7 500); δ_H (400MHz; CD_3CN) 1.78-1.97 (6H, m, $CH_2CH_2CH_2CH_2CH_2$), 3.33 (2H, m, CH_2CH_2Ar), 4.80 (2H, m, $CH_2CH_2N^+$), 7.87 (1H, m, C3-*H*), 7.95 (1H, d, *J* 7.8Hz, C1-*H*), 8.42 (1H, m, C2-*H*) and 8.86 (1H, d, *J* 5.5Hz, C4-*H*); δ_C (100MHz; CD_3CN) 25.2, 27.3, 29.1, 35.0, 62.7, 126.9, 130.4, 146.8 and 161.3; *m/z* (200°C) 148 (M^+-I, 22%) and 93 (100).

4-Methyl 7,8,9,10-tetrahydro-6H-pyrido[1,2-a]azepinium iodide (**26**)

Obtained from 1-(5-iodopentyl) 2-methylpyridinium iodide (**22**) as an orange solid (58%; dec. > 140°C) (Found: C, 45.85; H, 5.88; N, 4.77%. $C_{11}H_{16}NI$ requires C, 45.69; H, 5.58; N, 4.84%); υ_{max} (KBr disc) 3 015, 2 932, 2 858, 1 621, 1 583 and 1 489cm^{-1}; λ_{max} (EtOH) 218 nm (ε 19 000) and 276 (7 800); δ_H (400MHz; CD_3CN) 1.80-1.98 (6H, m, $CH_2CH_2CH_2CH_2CH_2$), 2.83 (3H, s, $ArCH_3$), 3.36 (2H, m, CH_2CH_2Ar), 4.68 (2H, m, $CH_2CH_2N^+$), 7.76 (2H, m, C1-*H* and C3-*H*) and 8.23 (1H, t, *J* 7.9Hz, C2-*H*); δ_C (100MHz; CD_3CN) 22.6, 25.5, 25.7, 28.7, 35.3, 35.2, 128.0, 129.0, 145.7, 156.5 and 161.7; *m/z* (200°C) 162 (M^+-I, 14%) and 107 (100).

2-Methyl 7,8,9,10-tetrahydro-6H-pyrido[1,2-a]azepinium iodide (**27**)

Obtained from 1-(5-iodopentyl) 4-methylpyridinium iodide (**23**) as a light brown solid (79%; m.p. 100-101°C) (Found: C, 45.57; H, 5.73; N, 4.75%. $C_{11}H_{16}NI$ requires C, 45.69; H, 5.58; N, 4.84%); υ_{max} (KBr disc) 3 011, 2 932, 2 854, 1 640, 1 573 and 1 520cm^{-1}; λ_{max} (EtOH) 220 nm (ε 21 500) and 264 (6 100); δ_H (400MHz; CD_3CN) 1.77-1.98 (6H, m, $CH_2CH_2CH_2CH_2CH_2$), 2.58 (3H, s, $ArCH_3$), 3.26 (2H, m, CH_2CH_2Ar), 4.73 (2H, m, $CH_2CH_2N^+$), 7.67 (1H, m, C3-*H*), 7.79 (1H, s, C1-*H*) and 8.70 (1H, d, *J* 6.4Hz, C4-*H*); δ_C (100MHz; CD_3CN) 22.0, 25.5, 27.6, 29.2, 34.9, 61.9, 127.3, 130.7, 145.8, 160.0 and 160.6; *m/z* (200°C) 162 (M^+-I, 24%) and 161 (100).

1,3-Dimethyl 7,8,9,10-tetrahydro-6H-pyrido[1,2-a]azepinium iodide (**28**)

Obtained from 1-(5-iodopentyl) 3,5-dimethylpyridinium iodide (**24**) as a white solid (66%; m.p. 151-152°C) (Found: C, 47.53; H, 6.20; N, 4.73%. $C_{12}H_{18}NI$ requires C, 47.54; H, 5.98; N, 4.62%); υ_{max} (KBr disc) 2 933, 2 862, 1 628 and 1 514cm^{-1}; λ_{max} (EtOH) 219 nm (ε 24 100) and 280 (9 100); δ_H (400MHz; CD_3CN) 1.74-1.98 (6H, m, $CH_2CH_2CH_2CH_2CH_2$), 2.43 (3H, s, $ArCH_3$), 2.50 (3H, s, $ArCH_3$), 3.25 (2H, m, CH_2CH_2Ar), 4.78 (2H, m, $CH_2CH_2N^+$), 8.16 (1H, s, C2-*H*) and 8.69 (1H, s, C4-*H*); δ_C (100MHz; CD_3CN) 17.9, 20.1, 24.2, 27.5, 28.9, 29.6, 62.3, 136.7, 138.2, 144.1, 148.1 and 157.1; *m/z* (200°C) 176 (M^+-I, 14%) and 121 (100).

Treatment of 1-(10-iododecyl)pyridinium iodide (**31**) ***with tri-n-butyltin hydride and AIBN***

The reaction was carried out according to the general procedure using 2 equivalents of AIBN. After partitioning, the crude product was chromatographed on silica with EtOAc/MeOH (5:2) to afford 1-decylpyridinium iodide[12] as a yellow gum (30%); υ_{max} ($CHCl_3$ soln) 2 932, 2 858, 1 636 and 1 487 cm^{-1}; λ_{max} (EtOH) 220 nm (ε 18 000) and 259 (3 800); δ_H (250MHz; CD_3OD) 0.89 (3H, t, *J* 6.6Hz, CH_2CH_3), 1.28-1.39 (12H, m, 6 x $CH_2CH_2CH_2$), 2.04 (2H, m, $CH_2CH_2CH_2$), 4.68 (2H, t, *J* 7.6Hz, $CH_2CH_2N^+$), 8.14 (2H, m, C3-*H* and C5-*H* (ring)), 8.62 (1H, m, C4-*H* (ring)) and 9.08 (2H, d, *J* 5.5Hz, C2-*H* and C6-*H* (ring)); δ_C (100MHz; CD_3OD) 14.4, 23.7, 27.2, 30.1, 30.4, 30.5, 30.6, 32.5, 33.0, 63.1, 129.5, 146.0 and 146.9;*m/z* (F.A.B.,+ve ion;MNBA) 567 ([2*M*-I]$^+$, 1%) and 220 ([*M*-I]$^+$).