Intramolecular Vilsmeier processes: a new route to cyclopenta[*b*]- and cyclohexa[*b*]-fused quinolines by cyclisation of adipic and pimelic bis-amides

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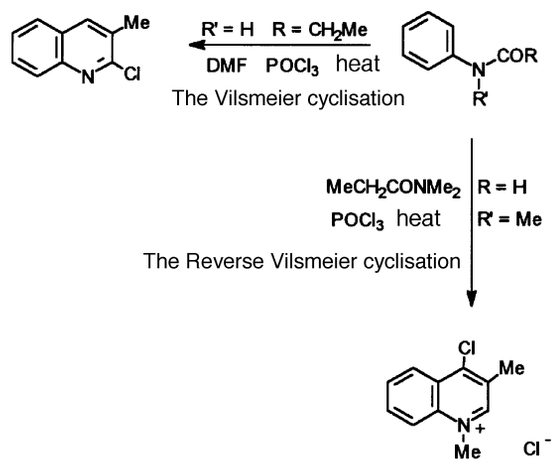
Symmetrical and unsymmetrical bis-amides derived from adipic and pimelic acid and secondary amines react in $POCl_3$ solution to give the title compounds by way of a Vilsmeier reagent–α-chloro enamine interaction. Adipanilide and pimelanilide only cyclise with added PCl_5. However the bis-*N*-substituted derivatives (*N*-methyl or *N*-phenyl) of adipanilide and pimelanilide give quinolinium salts in good yield. Unsymmetrical amides with an *N*-substituted anilide at one end and an aliphatic unit at the other only proceed as far as the intermediate stage, giving 1,2-disubstituted cyclo-pentanes or -hexanes. Analogous amides derived from suberic and sebacic acid do not give quinolinium salts but instead give complex mixtures.

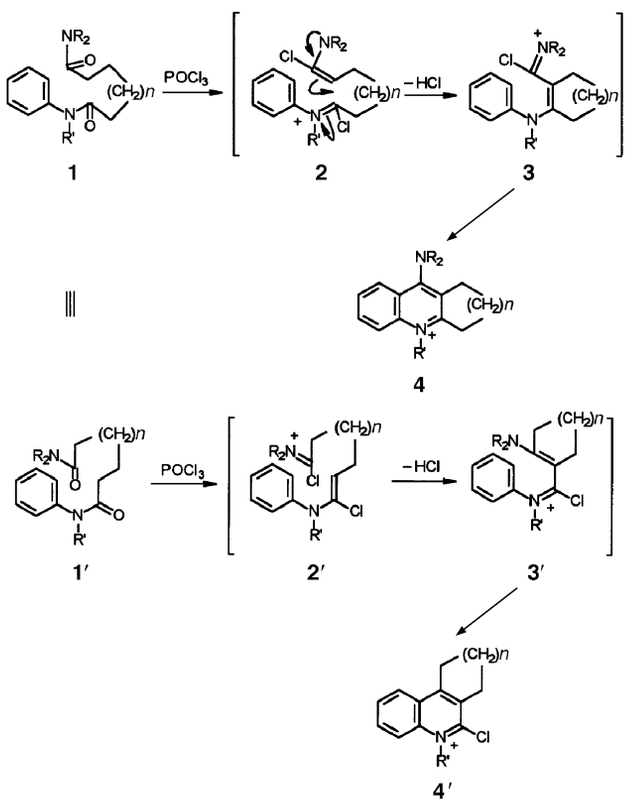
Introduction

In past publications we have disclosed two types of quinoline-forming reactions: the Vilsmeier cyclisation[1] involves the interaction of an acylanilide with dimethylformamide (DMF) in $POCl_3$. The Reverse Vilsmeier cyclisation[2] utilises the interaction of *N*-alkylformanilides with, for example, a tertiary amide (Scheme 1). These versatile processes involve in each case



Scheme 1

the interaction of two amides in $POCl_3$ solution, one being a formamide and a source of a Vilsmeier reagent. The Vilsmeier reagent generates the 4-carbon in the former case and all but the 3,4-carbons in the latter. In this paper we examine the intramolecular interaction of α,ω-diamides in $POCl_3$, posing the question: can we observe an intramolecular combination of the two above reaction types? Symmetrical α,ω-diamides were made by standard methods while unsymmetrical α,ω-diamides were made using acid–amine coupling with 1,3-dicyclohexylcarbodiimide (DCC) or 1-methyl-2-chloropyridinium salts.[3] Both of the above quinoline-forming reactions involve the interaction of an iminium salt (derived from the formamide component) with an α-chloro enamine (derived from the other amide) in $POCl_3$ as solvent. The reaction progress was thus easily monitored by ^1H NMR spectroscopy. Conceptually, the intramolecular process can follow two possible pathways, giving a linear **4** or an angular cyclisation product **4′** in the case of an arylamide (Scheme 2 shows a typical case). Given a symmetrical bis-amide, **3** and **3′** are potentially interconvertible geometric isomers.

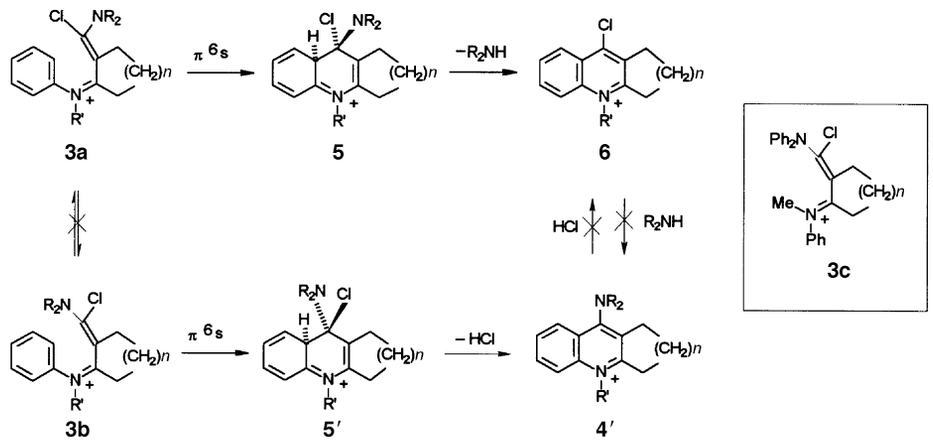


Scheme 2 The linear and angular pathways for diamide cyclisations

The reaction does indeed work to yield solely the linear products but is limited to adipic and pimelic acid derivatives, higher analogues giving complex mixtures and no quinolinium salts.

Results and discussion

We have examined the reaction as a function of (a) chain length, (b) variation of the amide termini from symmetrical to non-symmetrical units, (c) variation of the amide termini from dialkylamino to cyclic alkylamino (*e.g.* piperidino) to alkylarylamino and diarylamino groups and (d) the use of tertiary or secondary amides. The products were precipitated by aqueous quenching followed by addition of ammonium hexafluorophosphate and ethyl acetate. Several noteworthy features deserve comment.



n = 1 or 2; for R and R′ see text

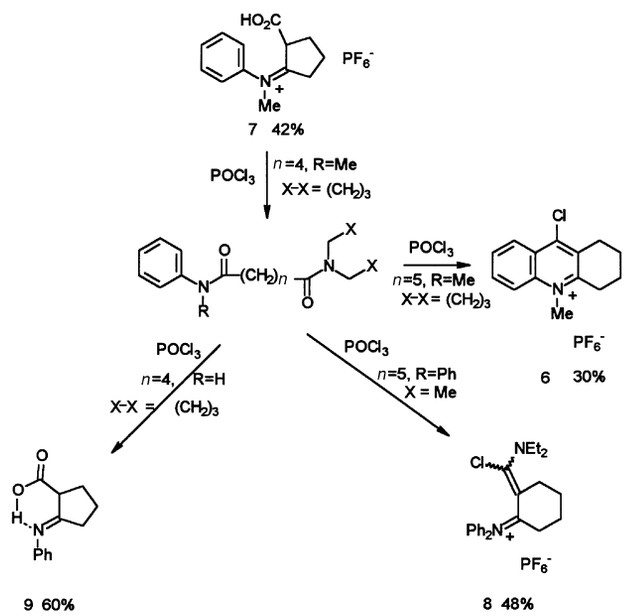
Scheme 3

(1) In all cases examined so far, only adipic and pimelic acid derivatives gave cyclisation products; suberic, sebacic and dodecanoic acid amides gave complex mixtures and no salts were precipitated. Attainment of the correct cyclisation geometry appears to be problematic for the higher homologues due to bulky terminal groups and medium/large sized ring effects.

(2) All cyclisations gave linear rather than angular tricyclic products. This was demonstrated by difference NOE studies of the products **4** (in particular those derived from bis-*N*-methylanilides, which showed strong interactions between the pyridinium ring *N*-substituent and the adjacent aliphatic and aromatic ring protons, which would not be observed for the angular products). The geometry leading to the tricycle from the intermediate is clearly more hindered for the angular product **4′** formation, where cyclisation is impeded by the NR_2 group (Scheme 2).

(3) In most cases a 9-disubstituted amino-derivative **4** was formed. However, the bis-*N*,*N*-diphenylamide of pimelic acid produced both the 9-chloro derivative **6** and the 9-amino derivative **4**, the ratio being dependent upon the time of heating. The yield of the 9-chloro derivative (18% ± 1) remained essentially constant while that of the 9-diphenylamino derivative increased from 18% after 1 h to 39% after 20 h of heating. The 9-chloro and 9-diphenylamino derivatives did not interconvert under the reaction conditions. If we assume the cyclisation mechanism is related to that published for the quinolinium salt formation,[2] the two geometries of the precursor cycloalkane **3a** and **3b** (Scheme 3) cyclise by a $_{\pi}6_{s}$ mechanism. Disrotatory motion of the cyclising termini followed by *trans*-elimination of HX yields the acridinium salt. However, the greater steric barrier to cyclisation of **3b** which leads to the 9-diphenylamino derivative results in a significantly slower cyclisation. Surprisingly, the isomers **3a** and **3b** do not appear to interconvert under the reaction conditions. Furthermore, only the diphenylamino product **4** (*n* = 1), was isolated from the corresponding adipamide. Traces of the 9-chloro-10-phenyltetrahydroacridone were formed (as indicated by electrospray MS) when *N*-methyl-*N*,*N*′,*N*′-triphenylpimelamide were similarly cyclised, together with an inseparable *ca.* 2 : 1 mixture of the 9-diphenylamino-10-methyl- and 9-methylanilino-10-phenyltetrahydroacridines **4**. This preference is to be expected since the intermediate leading to the latter product would tend to exist in a 'non-cyclising' geometry, **3c**, with the large groups *exo*.

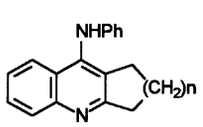
(4) Symmetrical bis-amides (*e.g.* bis-*N*-methylanilides and *N*,*N*-diphenylamides) gave the highest yields and reaction rates. In contrast, unsymmetrical amides not only gave lower yields and reaction rates but tended to give intermediate products such as **7** or **8** (drawn as its most probable geometric isomer) indicative of the fact that the former series had double the opportunity to to attain cyclisation geometry. The transition state energy for



Scheme 4

further cyclisation is, apparently, too high (Scheme 4). With one pimelic amide, $PhMeNCO(CH_2)_5CON(CH_2)_5$, the chloroacridinium salt **6** was formed with no sign of the corresponding piperidino acridinium salt. The 9-chloro-10-methyl- or -10-phenyl-tetrahydroacridinium salts **6** were prepared unambiguously in two steps by Reed's method[4] (see Experimental section) for comparison.

(5) We also examined the cyclisation of adipic and pimelic aniliides, $PhNHCO(CH_2)_nCONHPh$. Although they were unchanged under the conditions utilised above, von Braun noted during his classical investigation of the effect of PCl_5 on amides that poor yields of fused quinolines were formed from these amides.[5] Clearly the intermediate equivalent to the Vilsmeier reagent derived from a secondary amide is much less reactive than that derived from a tertiary amide. However, using the more potent Lewis acid system of $POCl_3$–PCl_5 with NMR optimisation, efficient cyclisation was observed with both adipic and pimelic amides to give the fused quinolines **10**. How-



10a *n* = 1; **b** *n* = 2

ever, when the adipamide, $(CH_2)_5NCO(CH_2)_4CONHPh$ was similarly treated, once again only an intermediate **9** was isolated.

Experimental

Melting points were conducted on a Reichert Kofler hot-stage apparatus. IR spectra were obtained on a Unicam Research Series 1 FTIR instrument as liquid films or KBr discs. NMR spectra were recorded in $CDCl_3$ or for the salts in [$^2H_6$]acetone solution with tetramethylsilane as internal standard on a JEOL 270 (^{1}H, 270 MHz; ^{13}C, 67.5 MHz), while reaction monitoring by NMR was conducted on a Perkin-Elmer R 24B. *J* Values are in Hz. Mass spectra were obtained with a Kratos MS8ORF or a VG Trio 2000 mass spectrometer (using electrospray injection for the salts) and microanalyses were carried out at Newcastle University on a Carlo Erba 1106 Elemental Analyser. Thin layer chromatography (TLC) were performed with Merck silica 60 F254 plates and for flash chromatography Janssen silica (35–70 μm) was used with ethyl acetate–light petroleum elution. Light petroleum refers to that of bp 60–80 °C and ether implies diethyl ether. The following known diamides were made by the literature method: Adipamides; *N*,*N*′-diphenyl,[6] *N*,*N*′-dimethyl-*N*,*N*′-diphenyl[7] and ethyl adipamate.[8] Pimelamide: *N*,*N*′-diphenyl;[9] suberamides: *N*,*N*′-diphenyl,[9] *N*,*N*′-dimethyl-*N*,*N*′-diphenyl.[9]

General methods for the preparation of symmetrical diamides

The appropriate acid chloride (50 mmol) was added dropwise to the amine (100 mmol) in pyridine (*ca*. 10 ml) at ambient temperature and the mixture was heated at 90 °C for 1 h; it was then poured into water and the product extracted with dichloromethane. The organic phase was washed successively with water, hydrochloric acid (1 M; × 3), water and aqueous sodium carbonate (1 M; × 2), dried ($MgSO_4$) and evaporated. The resulting product was either recrystallised or chromatographed to give the following products.

***N*,*N*′-Dimethyl-*N*,*N*′-diphenylpimelamide 1 (R_2 = Me and Ph, R′ = Me, *n* = 2)** as a pale yellow oil; $\delta_H(CDCl_3)$ 1.11 (2 H, quin, *J* 6.5, mid-CH_2), 1.48 (4 H, quin, *J* 7.4, $COCH_2CH_2$'s); 2.01 (4 H, t, *J* 7.4, $COCH_2$'s), 3.24 (6 H, s, Me's) and 7.13–7.44 (10 H, m); ν_{max}/cm^{-1} 1658, 758 and 701 (Found: *m*/*z* 338.1986. $C_{21}H_{26}N_2O_2$ requires 338.1994).

***N*,*N*′-Dimethyl-*N*,*N*′-diphenylsebacamide 1 (R_2 = Me and Ph, R′ = Me, *n* = 5)** as white cuboids from ethyl acetate–light petroleum, mp 85–86 °C (Found: C, 75.87; H, 8.71; N, 7.30. $C_{24}H_{32}N_2O_2$ requires C, 75.75; H, 8.48; N, 7.36%); $\delta_H(CDCl_3)$ 1.11 (8 H, m, mid-CH_2's), 1.51 (4 H, quin, *J* 7.4, $COCH_2CH_2$'s), 2.03 (4 H, t, *J* 7.4, $COCH_2$'s), 3.25 (6 H, s, Me) and 7.15–7.45 (10 H, m); ν_{max}/cm^{-1} 1664, 782 and 703; *m*/*z* 380 (M^+).

***N*,*N*,*N*′,*N*′-Tetraphenyladipamide 1 (R = R′ = Ph, *n* = 1)** as white needles from ethanol, mp 137–138 °C (Found: C, 80.20; H, 6.43; N, 6.16. $C_{30}H_{28}N_2O_2$ requires C, 80.33; H, 6.29; N, 6.25%); $\delta_H(CDCl_3)$ 1.63 (4 H, m, $COCH_2$'s), 2.20 (4 H, m, mid-CH_2's), 7.26 (8 H, m) and 7.33 (12 H, m); ν_{max}/cm^{-1} 1675, 754 and 698; *m*/*z* 448 (M^+).

***N*,*N*,*N*′,*N*′-Tetraphenylpimelamide 1 (R = R′ = Ph, *n* = 2)** as white needles from ethanol, mp 140–141 °C (Found: C, 80.31; H, 6.52; N, 5.97. $C_{31}H_{30}N_2O_2$ requires C, 80.49; H, 6.54; N, 6.06%); $\delta_H(CDCl_3)$ 1.26 (2 H, quin, *J* 7.6, mid-CH_2), 1.59 (4 H, m, $COCH_2CH_2$'s), 2.22 (4 H, t, *J* 7.4, $COCH_2$'s) and 7.2–7.35 (20 H, m, ArH's); ν_{max}/cm^{-1} 1673, 759 and 703; *m*/*z* 462 (M^+).

***N*,*N*,*N*′,*N*′-Tetraphenylsuberamide 1 (R = R′ = Ph, *n* = 3)** as white needles from aqueous ethanol, mp 135 °C (Found: C, 80.39; H, 6.63; N, 5.79. $C_{32}H_{32}N_2O_2$ requires C, 80.64; H, 6.77; N, 5.88%); $\delta_H(CDCl_3)$ 1.24 (4 H, m, mid-CH_2's), 1.61 (4 H, m, $COCH_2CH_2$'s), 2.20 (4 H, t, *J* 7.6, $COCH_2$'s), 7.25 (8 H, d, *J* 7.4) and 7.35 (12 H, t, *J* 7.3); ν_{max}/cm^{-1} 1687, 755 and 694; *m*/*z* 476 (M^+).

Methods for the preparation of unsymmetrical diamides

(i) Ethyl adipoyl or ethyl pimeloyl chloride (50 mmol) was added dropwise with stirring to a solution of the appropriate amine (50 mmol) in pyridine (10 ml) at ambient temperature. After a further 1 h at 90 °C the mixture was quenched in water (*ca*. 50 ml) and extracted with ether. The organic extract was washed with hydrochloric acid (1 M; 2 × 25 ml), water and aqueous sodium carbonate (1 M; 2 × 25 ml), dried ($MgSO_4$) and evaporated. The products (30 mmol) resulting from interaction with aniline, *N*-methylaniline and diphenylamine (75–97%) in ethanol (20 ml) were each treated with lithium hydroxide (2.10 g, 50 mmol) in water (80 ml) with stirring for 12 h at ambient temperature. After neutralisation with hydrochloric acid (1 M) the mixture was extracted with dichloromethane and the extract dried ($MgSO_4$) and evaporated to give the corresponding amino acids (73–97%) which were used directly.

(ii) General method for amide formation using dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole. A mixture of the acid (10 mmol), 1-hydroxybenzotriazole (1.35 g, 10 mmol), piperidine (0.85 g, 10 mmol) and DCC (2.06 g, 11 mmol) in dry dichloromethane (50 ml) was stirred at ambient temperature for 1 h after which it was filtered and then evaporated. The product was obtained from the resulting residue by flash chromatography.

(iii) General method for amide formation using 1-methyl-2-chloropyridinium iodide. A mixture of the above amino acids (10 mmol), 1-methyl-2-chloropyridinium iodide (3.06 g, 12 mmol), tributylamine (4.45 g, 24 mmol) and the appropriate amine (10 mmol) in dichloromethane (50 ml) were stirred under nitrogen for 5 min at ambient temperature and then refluxed for 2 h. The reaction mixture was then diluted with ether and any precipitate filtered off and discarded. The filtrate was washed with hydrochloric acid (2 M; 3 × 50 ml) and water, dried ($MgSO_4$) and evaporated. The remaining product was purified by crystallisation as follows.

***N*-Phenyl-*N*′,*N*′-pentamethyleneadipamide 1 [R_2 = $(CH_2)_5$, R′ = H, *n* = 1; Method (ii)] (66%)** as white needles from ethyl acetate–light petroleum, mp 99–100 °C (Found: C, 70.80; H, 8.39; N, 9.71. $C_{17}H_{24}N_2O_2$ requires C, 70.65; H, 8.42; N, 9.57%); $\delta_H(CDCl_3)$ 1.55 [6 H, m, 3,4,5-$(CH_2)_3$ of piperidine], 1.75 (4 H, m, $COCH_2CH_2$'s), 2.40 (4 H, m, $COCH_2$'s), 3.40 (2 H, t, *J* 5.3, *N*-CH_2), 3.57 (2 H, t, *J* 5.5, *N*-CH_2), 7.07 (1 H, t, *J* 7.3, Ar-4-H), 7.29 (2 H, t, *J* 8.1, Ar-3,5-H) and 7.62 (2 H, d, *J* 7.6, Ar-2,6-H); ν_{max}cm/$^{-1}$ 3307, 1689, 1629 and 701; *m*/*z* 288 (M^+).

***N*-Methyl-*N*-phenyl-*N*′,*N*′-pentamethyleneadipamide 1 [R_2 = $(CH_2)_2$, R′ = Me, *n* = 1; Method (ii)] (84%)** as a pale yellow oil (Found: *m*/*z* 302.1998. $C_{18}H_{26}N_2O_2$ requires 302.1994); $\delta_H(CDCl_3)$ 1.61 [10 H, m, $COCH_2CH_2$'s and 3,4,5-$(CH_2)_3$ of piperidine], 2.10 (2 H, t, *J* 6.9, $COCH_2$), 2.24 (2 H, t, *J* 7.3, $COCH_2$), 3.26 (3 H, s, Me), 3.35 (2 H, t, *J* 5.3, *N*-CH_2), 3.51 (2 H, t, *J* 5.5, N-CH_2), 7.18 (2 H, d, *J* 7.0) and 7.39 (3 H, t, *J* 7.6), ν_{max}/cm^{-1} 1651, 775 and 701; *m*/*z* 302 (M^+).

***N*-Methyl-*N*-phenyl-*N*′,*N*′-pentamethylenepimelamide 1 [R_2 = $(CH_2)_5$, R′ = Me, *n* = 2; Method (ii)] (64%)** as a pale yellow oil (Found: *m*/*z* 316.2142. $C_{19}H_{28}N_2O_2$ requires 316.2151); $\delta_H(CDCl_3)$ 1.23 (2 H, quin, *J* 6.8, mid-CH_2), 1.53 [10 H, m, $COCH_2CH_2$'s and 3,4,5-$(CH_2)_3$ of piperidine], 2.08 (2 H, t, *J* 7.8, $COCH_2$), 2.27 (2 H, t, *J* 7.8, $COCH_2$), 3.26 (3 H, s, Me), 3.36 (2 H, t, *J* 5.3, N-CH_2), 3.52 (2 H, t, *J* 5.4, *N*-CH_2), 7.17 (2 H, d, *J* 7.6) and 7.40 (3 H, t, *J* 8.2); ν_{max}/cm^{-1} 1648, 775 and 701; *m*/*z* 316 (M^+).

***N*-Methyl-*N*,*N*′,*N*′-triphenylpimelamide 1 [R = Ph, R′ = Me, *n* = 2; Method (iii)] (90%)** as white needles from ethyl acetate–light petroleum, mp 90–91 °C (Found: C, 77.69; H, 7.09; N, 6.83. $C_{26}H_{28}N_2O_2$ requires C, 77.97; H, 7.05; N, 6.99%); $\delta_H(CDCl_3)$ 1.20 (2 H, m, mid-CH_2), 1.49 (4 H, m, $COCH_2CH_2$'s), 2.03 (2 H, t, *J* 7.4, $COCH_2$), 3.20 (2 H, t, *J* 7.7, $COCH_2$), 3.24 (3 H, s, Me) and 7.1–7.43 (15 H, m, ArH's); ν_{max}/cm^{-1} 1662 and 705; *m*/*z* 400 (M^+).

***N*,*N*-Diphenyl-*N*′,*N*′-diethylpimelamide 1 [R = Et, R′ = Ph, *n* = 2; Method (iii)] (84%)** as a pale yellow oil (Found: *m*/*z* 366.2291. $C_{23}H_{30}N_2O_2$ requires 366.2307); $\delta_H(CDCl_3)$ 1.09 (3 H,

t, *J* 7.3, Me), 1.15 (3 H, t, *J* 7.3, Me), 1.35 (2 H, m, $COCH_2$-CH_2CH_2), 1.65 (4 H, m, $COCH_2CH_2$'s), 3.28 (2 H, q, *J* 7.3, NCH_2CH_3), 3.35 (2 H, q, *J* 7.3, NCH_2CH_3), 2.27 (4 H, 2 overlapping t's, *J* 7.4 and 6.6, $NCOCH_2$'s) and 7.22–7.43 (10 H, m, ArH's); ν_{max}/cm^{-1} 2933, 1671, 1639, 1490, 757 and 703.

Reaction of diamides with $POCl_3$

Method 1: for tertiary diamides. The diamide (5 mmol) in $POCl_3$ (5 ml) was heated and stirred at 80 °C while a small aliquot in an NMR tube was monitored by ^{1}H NMR spectroscopy. Upon completion of the reaction the solution was carefully quenched in ice–water and treated with ethyl acetate and ammonium hexafluorophosphate (0.82 g, 5 mmol). The precipitate was recovered, washed with water and ether and recrystallised to give the products indicated below.

9-(*N*-Methylanilino)-4-methylcyclopenta[*b*]quinolinium hexafluorophosphate 4 (R_2 = Ph, Me, R′ = Me, *n* = 1). From *N*,*N*′-dimethyl-*N*,*N*′-diphenyladipamide was obtained after a reaction time of 45 min the title product (74%) as orange needles from ethanol, mp 189.5–190 °C (Found: C, 55.55; H, 4.64; N, 6.31. $C_{20}H_{21}N_2PF_6$ requires C, 55.30; H, 4.87; N, 6.45%); δ_H([$^2H_6$]acetone) 2.09 (3 H, s, 9-NMe), 2.31 (2 H, quin, *J* 7.6, 2-CH_2), 2.84 (2 H, t, *J* 7.0, 1-CH_2), 3.70 (2 H, t, *J* 7.8, 3-CH_2), 4.54 (3 H, s, 4-Me), 7.07 (3 H, m, *ortho* and *para* H's of Ph), 7.35 (2 H, t, *J* 8.0, *meta* H's of Ph), 7.84 (1 H, dt, 6-H), 7.84 (1 H, dt, 7-H), 8.30 (1 H, dd, *J* 8.4, 2.0, 8-H) and 8.75 (1 H, d, *J* 8.4, 5-H); ν_{max}/cm^{-1} 1592, 1398 and 838; *m*/*z* 289 (M^+ of cation).

10-Methyl-9-(*N*-methylanilino)-1,2,3,4-tetrahydroacridinium hexafluorophosphate 4 (R_2 = Ph,Me, R′ = Me; *n* = 2). From *N*,*N*′-dimethyl-*N*,*N*′-diphenylpimelamide was obtained after a reaction time of 1.5 h the title product (90%) as orange needles from ethanol, mp 231 °C (Found: C, 56.52; H, 4.68; N, 6.16. $C_{21}H_{23}N_2PF_6$ requires C 56.23; H 5.17; N 6.25%); δ_H([$^2H_6$]acetone) 1.93 (2 H, m, 2-CH_2), 2.15 (2 H, m, 3-CH_2), 2.85 (2 H, t, *J* 6.5, 1-CH_2), 2.97 (3 H, s, 10-NMe), 3.68 (2 H, t, *J* 6.5, 4-CH_2), 4.73 (3 H, s, 5-NMe), 6.84 (2 H, d, *J* 8.1, *ortho* H's of Ph), 6.99 (1 H, t, *J* 7.4, *para* H of Ph), 7.35 (2 H, dt, *J* 7.4 and 8.1, *meta* H's of Ph), 7.97 (1 H, dt, 7-H), 8.26 (2 H, 8- and 9-H) and 8.73 (1 H, d, *J* 9.2, 6-H); ν_{max}/cm^{-1}; *m*/*z* 303 (M^+ of cation).

9-Diphenylamino-4-phenylcyclopenta[*b*]quinolinium hexafluorophosphate 4 (R = R′ = Ph, *n* = 1). From *N*,*N*,*N*′,*N*′-tetraphenyladipamide after a reaction time of 4 h was obtained the title product (98%) as orange needles from ethyl acetate–light petroleum, mp 168–169 °C (Found: C, 64.30; H, 4.74; N, 4.77. $C_{30}H_{25}N_2PF_6$ requires C, 64.52; H, 4.51; N, 5.02%); δ_H([$^2H_6$]acetone) 2.23 (2 H, quin, *J* 7.4, 2-CH_2), 2.61 (2 H, t, *J* 7.4, 1-CH_2), 3.17 (2 H, t, *J* 7.4, 3-CH_2) and 7.3–8.1 (19 H, m, ArH's); ν_{max}/cm^{-1} 1583, 1394 and 838; *m*/*z* 413 (M^+ of cation).

9-Diphenylamino-10-phenyl-1,2,3,4-tetrahydroacridinium hexafluorophosphate 4 (R = R′ = Ph, *n* = 2). From *N*,*N*,*N*′,*N*′-tetraphenylpimelamide was obtained a mixture of two products; first, the title product as orange needles from ethanol, mp 215 °C (Found: C, 64.86; H, 4.68; N, 4.76. $C_{31}H_{27}N_2PF_6$ requires C, 65.03; H, 4.75; N, 4.89%); δ_H([$^2H_6$]acetone) 1.91 (4 H, br, 2,3-CH_2's), 2.61 (2 H, br, 1-CH_2), 3.04 (2 H, m, 4-CH_2) and 7.2–8.3 (19 H, m, ArH's); ν_{max}/cm^{-1} and 1490; *m*/*z* 427 (M^+ of cation). Depending upon time of heating the yield of this compound varied as follows: 1 h 18%; 4 h 34%; 7 h 34%; 20 h 39%. A second product, 9-chloro-10-phenyl-1,2,3,4-tetrahydroacridinium hexafluorophosphate **4** (R′ = Ph, *n* = 2) was observed in the NMR and mass spectra, but not separated, in the following yields: 1 h 18%; 4 h 18%; 7 h 17%; 20 h 19%; δ_H([$^2H_6$]acetone) 2.20 (4 H, br, 2,3-CH_2's), 3.20 (2 H, br, 1-CH_2), 3.75 (2 H, m, 4-CH_2) and 7.2–8.7 (19 H, m, ArH's); *m*/*z* 296/294 (M^+ of cation).

This second compound was also made as follows: *N*-Phenyl-1,2,3,4-tetrahydroacridin-9-one was made by Reed's method.[4] This acridone (1.26 g, 4.6 mmol) in $POCl_3$ (5 ml) was heated at 80 °C for 45 min and then poured onto ice–water to which ammonium hexafluorophosphate (0.82 g, 5 mmol) was subsequently added. The precipitate was filtered off, washed and dried to give the title solid (1.93 g, 96%).

Complex mixtures from which no salts were isolated resulted from similar reactions of *N*,*N*,*N*′,*N*′-tetraphenyl-suberamide and -dodecanoamide.

9-Chloro-10-methyl-1,2,3,4-tetrahydroacridinium hexafluorophosphate 6. From *N*′-methyl-*N*′-phenyl-*N*,*N*-pentamethylene-pimelamide after a reaction time of 6 h was obtained the title product (30%) as yellow needles from ethyl acetate–acetonitrile, mp 176–177 °C (Found: C, 44.55; H, 3.91; N, 3.79. $C_{14}H_{15}ClNPF_6$ requires C, 44.52; H, 4.00; N, 3.71%); δ_H([$^2H_6$]acetone) 1.99 (4 H, m, 2,3-CH_2's), 3.11 (2 H, t, *J* 6.6, 1-CH_2), 3.50 (2 H, t, *J* 6.3, 4-CH_2), 4.55 (3 H, s, NMe), 7.99 (1 H, dt, 6-H), 8.17 (1 H, dt, 7-H), 8.54 (1 H, dd, 8-H) and 8.57 (1 H, br d, 5-H); ν_{max}/cm^{-1} 1569 and 836; *m*/*z* 234/232 (M^+ of cation).

This compound was also made as follows *N*-Methyl-1,2,3,4-tetrahydroacridin-9-one was made by Reed's method.[4] This acridone (1.21 g, 6.7 mmol) in $POCl_3$ (5 ml) was heated at 80 °C for 45 min and then poured onto ice–water to which ammonium hexafluorophosphate (1.14 g, 7 mmol) was subsequently added. The precipitate was filtered off, washed and dried to give the title solid (1.85 g, 87%).

(A) 10-Methyl-9-diphenylamino-1,2,3,4-tetrahydroacridinium hexafluorophosphate 4 (R = Ph, R′ = Me, *n* = 2), (B) 9-*N*-methylanilino)-10-phenyl-1,2,3,4-tetrahydroacridinium hexafluorophosphate 4 (R_2 = Ph,Me, R′ = Ph, *n* = 2) in ratio ~2:1 (total yield 18%) and traces of (C) 10-phenyl-9-chloro-1,2,3,4-tetrahydroacridinium hexafluorophosphate 6 (R = Ph). From *N*-methyl-*N*,*N*′,*N*′-triphenylpimelamide was obtained after a reaction time of 6 h the title products as an inseparable orange solid; δ_H([$^2H_6$]acetone) 1.91 and 2.12 (m, 2,3-CH_2's of A and B), 2.60 (2 H, t, *J* 6.3, 1-CH_2 of A), 3.15 (3 H, s, NMe of B), 3.21 (2 H, m, 1-CH_2 of B), 3.64 (2 H, t, *J* 6.7, 4-CH_2 of A), 3.75 (2 H, m, 4-CH_2 of B), 4.69 (3 H, s, NMe of A) and 7.1–8.8 (m, ArH's); ν_{max}/cm^{-1} 1583, 1508, 1490, 844 and 833; *m*/*z* 365 and 296/294, respectively (M^+ of cations).

1-(1-Chloro-1-diethylaminomethylene)-2-(*N*-diphenyliminio)-cyclohexane hexafluorophosphate 8. From *N*,*N*-diethyl-*N*′,*N*′-diphenylpimelamide was obtained after a reaction time of 7 h the title product as a mixture of geometric isomers (48%) as yellow needles from ethyl acetate–acetonitrile, mp 158–159 °C (Found: C, 53.89; H, 5.43; N, 5.36. $C_{23}H_{28}ClN_2PF_6$ requires C, 53.86; H, 5.50; N, 5.46%); δ_H([$^2H_6$]acetone) 1.53 (6 H, m, 2-Me's), 1.75, 2.55, 2.60, 2.8, 3.10, 3.4, 3.5 and 3.85 (8 H, 8 × m) 4.19 (2 H, m, CH_2), 4.46 (2 H, m, CH_2), 7.20 (6 H, m, *ortho* and *para* H's of Ph's) and 7.44 (4 H, m, *meta* H's of Ph's); $\nu_{max}$$cm^{-1}$ 1490 and 835; *m*/*z* 369/367 (M^+ of cation).

Method 2: for secondary diamides The diamide (5 mmol), PCl_5 (2.09 g, 10 mmol) and $POCl_3$ (5 ml) were stirred together for 1 h and then heated at 80 °C for 30 min. The mixture was diluted with acetone (15 ml) and ether (*ca*. 50 ml). The precipitate was filtered off and dissolved in water (50 ml) and the solution was treated with aqueous sodium carbonate (20%; 20 ml) to liberate the quinoline derivatives below.

8-anilinocyclopenta[*b*]quinoline 10a (55%) as white needles from ethanol, mp 239–240 °C (lit.,[5] mp 240–241 °C).

9-Anilino-1,2,3,4-tetrahydroacridine 10b (97%) as white needles from ethanol, mp 231–232 °C (lit.,[5] mp 232 °C).

2-(*N*-Phenylimino)cyclopentanecarboxylic acid 9 (60%) as cream needles from ethyl acetate–light petroleum, mp 90–92 °C (Found: C, 70.55; H, 6.48; N, 6.86. $C_{12}H_{13}NO_2$ requires C 70.92; H, 6.45; N, 6.89%); δ_H($CDCl_3$) 1.88 (1 H, m, 4-CHa), 2.10 (1 H, m, 4-CHb), 2.38 (4 H, m, 3-CH_2's and 5-CH_2's), 3.17 (1 H, t, *J* 9.7, CH), 7.09 (1 H, tt, *J* 7.6, 1.2), 7.33 (2 H, t, *J* 8.6), 7.56 (2 H, br dd) and 8.75 (1 H, br, NH/OH); ν_{max}/cm^{-1} 1662 and 705; *m*/*z* 400 (M^+).

Treatment of the *N*,*N*′-diphenyl-suberamide, -sebacamide and -dodecanoamide under the above conditions gave complex mixtures from which no simple products were isolable.

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