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The Synthesis and Stereochemistry of Some New Medium-Ring Nitrogen-containing Alcohols and Related Compounds

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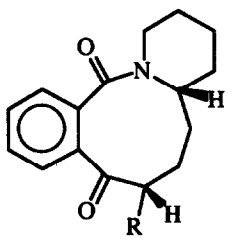
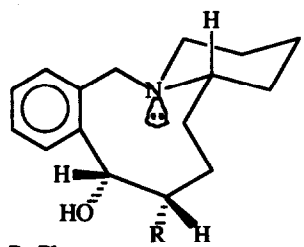
Abstract: Lithium aluminium hydride reduction of *rel*-(6*S*, 8a*R*)-6-*p*-chlorophenyl-6,7,8,8a,9,10,11,12-octahydropyrido[1,2-*b*][2]benzazonin-5,14-dione gave *trans*-fused *rel*-(5*S*, 6*S*, 8a*R*)-6-*p*-chlorophenyl and *cis*-fused *rel*-(5*R*, 6*S*, 8a*R*)-6-*p*-chlorophenyl-5,6,7,8,8a,9,10,11,12,14-decahydro[1,2-*b*][2]benzazonin-5-ol in equal amounts. Oxidation of *trans*-fused *rel*-(5*S*, 6*S*, 8a*R*)-6-phenyl-5,6,7,8,8a,9,10,11,12,14-decahydro[1,2-*b*][2]benzazonin-5-ol **3** gave *cis*-fused *rel*-(6*S*, 8a*R*)-6-phenyl-5,6,7,8,8a,9,10,11,12-octahydro[1,2-*b*][2]benzazonin-5-(14*H*)-one. Treatment of **3** with phosphorous oxychloride in pyridine yields *rel*-(4a*R*,7*R*,7a*R*,13*R*)1,2,3,4a,5,6,7,7a,12-decahydro-7-phenylisoindol-[1,2-*d*][2]quinolizin-13-ium phosphate (37%) by transannular reaction and *cis*-fused *rel*-(5*R*,6*R*,8a*R*)-6-phenyl-5,6,7,8,8a,9,10,11,12,14-decahydro[1,2-*b*][2]benzazonin-5-ol (11%) with a change in stereochemistry at C5 and C6.

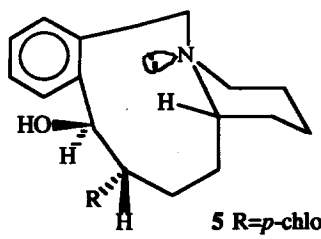
Medium-sized rings[1] are commonly found in many groups of natural products which possess wide and diverse medicinal and biological properties. In addition such systems incorporating a nitrogen atom at a ring fusion between six- and nine-membered rings can exist in several different conformations and these have received very little attention.[2]



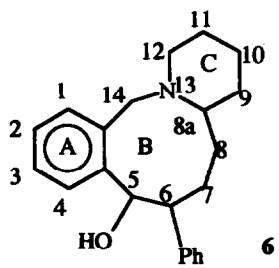
1 R=Ph
2 R=*p*-chlorophenyl



3 R=Ph
4 R=*p*-chlorophenyl



5 R=*p*-chlorophenyl



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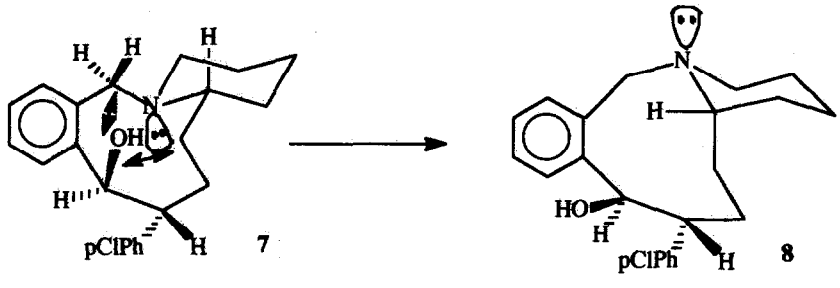
Previous attempts at the reduction of the carbonyl group of **1** yielded only one of the two possible epimeric alcohols *ie.* **3**.[2] When this reduction was performed with **2** both epimeric alcohols **4** and **5** were both obtained (in equal amounts, as judged by ^{1}H NMR) and separated by column chromatography. (Here it is possible that the *p*-chlorophenyl grouping causes a slight change in the conformation to that in **1** such that both prochiral faces of the carbonyl group become equally accessible to hydride reduction).

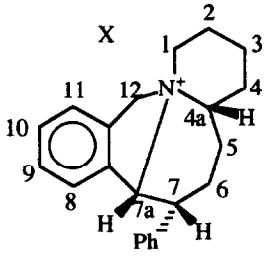
The first alcohol to be eluted from the column was identical to **3** in conformation and stereochemistry as judged by ^{1}H and ^{13}C NMR and is therefore assigned as *rel*-(5*S*,6*S*, 8a*R*)-6-*p*-chlorophenyl-5,6,7,8,8a,9,10,11,12,14-decahydropyrido[1,2-*b*][2]benzazonin-5-ol (See table 1). The second alcohol however possessed ^{1}H and ^{13}C NMR signals consistent with an isomeric alcohol but significantly different from the first eluted alcohol **4**. The ^{1}H NMR assignments of the signals to *H*-5, *H*-6, *H*-12eq and *H*-12ax were ascertained by ^{1}H NMR homonuclear decoupling techniques. Comparison of the *H*-5, *H*-6 coupling constants for the two alcohols obtained from the lithium aluminium hydride reduction of *rel*-(6*S*, 8a*R*)-6-*p*-chlorophenyl-6,7,8,8a,9,10,11,12-octahydropyrido[1,2-*b*][2]benzazonin-5,14-dione indicates the second alcohol is *rel*-(5*R*,6*S*,8a*R*)-6-*p*-chlorophenyl-5,6,7,8,8a,9,10,11,12,14-decahydropyrido[1,2-*b*][2]benzazonin-5-ol. However the difference in both the ^{13}C and ^{1}H NMR spectra of the second alcohol from the first also indicate different conformations, particularly considering the proton chemical shift differences of the C14 protons. Dreiding models of the second alcohol indicate an unfavourable steric interaction between the hydroxyl group and the C14/C8 protons indicated below **7**. This interaction is removed by nitrogen inversion and chair/chair interconversion of the piperidine ring to the *cis*-fused conformer **8**. This conversion to **8** causes two γ-axial effects operating between the C8 and the C10 and C12 carbon atoms, shielding these by *ca.* 4ppm. These observations are confirmed by the upfield shifts in the ^{13}C NMR signals for these carbon atoms. The stereochemistry and conformation of the second alcohol is thus that containing the *cis*-fused B/C ring fusion depicted in **8**.

Table 1 ^{13}C NMR Chemical Shifts

	C5	C6	C7	C8	C8a	C9	C10	C11	C12	C14
3	81.6	53.6	30.2	23.8	60	33	25.1	26.4	51	59.4
4	81.9	53	30	23.7	60	32	25	26.4	53.7	59.6
5	74.7	54.9	30.8	22.7	56	29.1	22.2	26.8	50.4	63.1
13	80.7	34.3	22	22.6	66.2	26.3	16.2	26.1	48.7	62.4
17	196	56.1	28.5	21.9	58.6	29.4	27.3	22.6	45.8	56.5

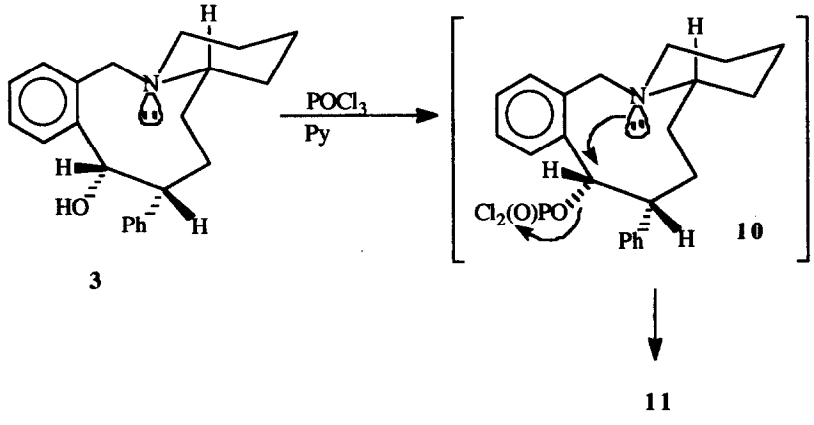


Since Sarret[3] has found that dehydration of selected steroidal alcohols to conjugated alkenes occurred readily when treated with phosphorus oxychloride in pyridine at room temperature this method was applied to alcohol **3**. Chromatography of the crude reaction mixture yielded two products in yields of 37% and 11%. The major product possessed complex ^{1}H and ^{13}C NMR spectra; however, they were similar to those in the tosylate **9** previously reported by us.[2,4] Examination of the ^{13}C NMR spectra indicated there was less than a 0.5ppm difference in chemical shifts for all the carbon atoms of the first product to that of the tosylate.[2] The product is thus assigned structure **11** differing only in the counterion present. (Lassaignes' test for phosphorus proved



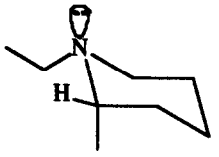
9 X=TsO^-
11 X=$H_2PO_4^-$

positive). Formation of **11** may occur as shown below. Treatment of the alcohol with phosphorus oxychloride in pyridine yields the intermediate phosphorus ester **10**. Transannular reaction then gives **11**, with concomitant hydrolysis of the counterion to phosphate.



The second product obtained in 11% yield was obtained in larger quantities by repeated reactions. Examination of the IR spectrum of this indicated a hydroxyl absorption at 3500cm^{-1} and mass spectral evidence indicated a molecular ion at (M^+) 321. In addition the ^{13}C NMR of **13** (table 1) suggested an isomer of **3**. The slightly broadened singlet for *H*-5 indicates a dihedral angle of *ca.* 90° between *H*-5 and *H*-6. The *H*-6 also resonates as a broad singlet and therefore the C6-*H* bond bisects the C7 methylene group. The C14 protons resonate at δ5.2 and δ5.3 (J_{gem}=-15.2Hz). The second most upfield methylene in the ^{13}C NMR spectrum at δ48.7 is likely to be the C12 methylene and $^{1}H/^{13}C$ NMR correlations indicate that the C12-*H*ax and C12-*H*eq protons resonate at δ2.6 and δ2.7. The one proton broadened singlet at δ5.3 correlates to the methine carbon atom at δ66.2 implicating the C8a bridgehead proton. Examination of the splittings of the C8a proton shows the absence of the large (10-12Hz) couplings expected for an axial proton and would suggest couplings of *ca.* 5-6Hz

indicative of an equatorial C8a bridgehead proton as shown below. In this *cis*-fused conformation of the piperidine the γ-axial effect operating between the C8 and C10 carbons is expected to give rise to absorption for C10 in the ^{13}C NMR spectrum of δ19ppm. A value of δ16.2 is observed providing evidence for this



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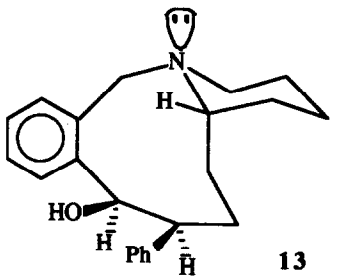
conformation. Dreiding models of the product with an axially substituted piperidine ring then allows the 5-hydroxyl and 6-phenyl groups to be placed with the correct dihedral angles between the C5-, C6-, and C7-protons as shown below. The product is thus assigned as *rel*-(5*R*,6*R*,8a*R*)-6-phenyl-5,6,7,8,8a,9,10,11,12,14-decahydropyrido[1,2-*b*][2]benzazonin-5-ol **13**. The change in *trans*-ring fusion of the alcohol **3** to the *cis*- in **13** and the change in stereochemistry of the 5-ol and 6-phenyl from *rel*-(5*S*,6*S*) to *rel*-(5*R*,6*R*) may occur as



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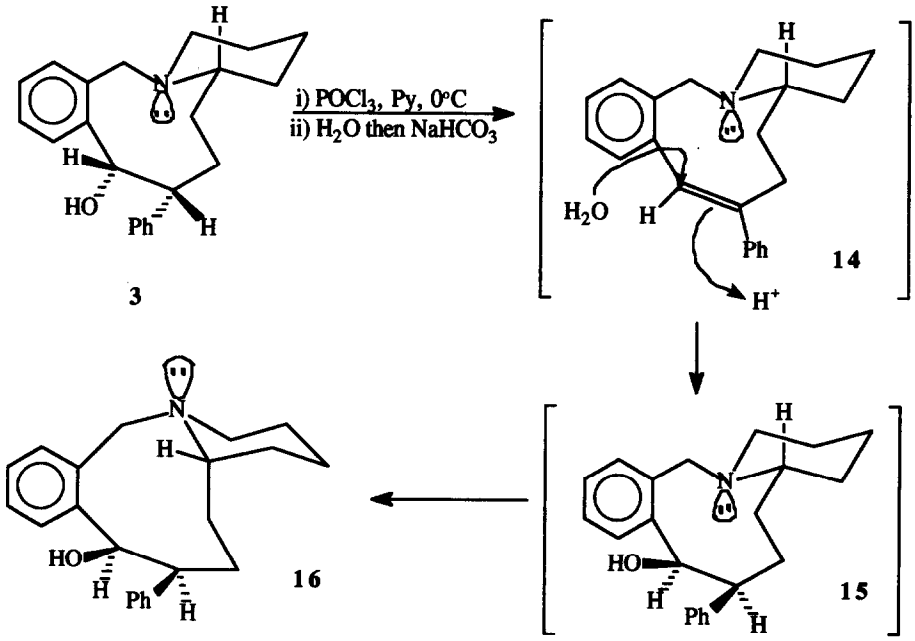
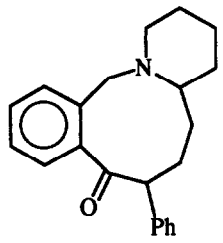
shown below. Dehydration of the alcohol **3** with phosphorus oxychloride in pyridine yields the strained Δ5-6



3 14 15 16

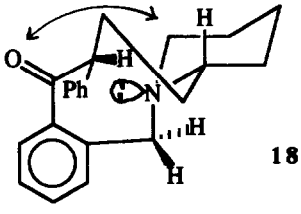
alkene **14** which then adds water as shown to give **15**. In this conformation however there exists steric repulsions between the C7 and C14 methylene protons and also between the 6-phenyl and C9 methylene groups. These interactions are partially relieved by nitrogen inversion and chair/chair interconversion of the piperidine ring to give *cis*-fused **16**.

We next turned our attention to the synthesis of the ketone *rel*-(6*S*, 8a*R*)-6-phenyl-6,7,8,8a,9,10,11,12-decahydro[1,2-*b*][2]benzazonin-5-(6*H*)-one **17**. Oxidation of the sp^3 hybridised alcohol group of **3** to the sp^2



17

hybridised group of **17** is predicted (by the use of Dreiding models) to produce a large change in the overall conformation from the 9-6 *trans*-fused system of **3**. Jones' oxidation of *rel*-(5*S*, 6*S*, 8a*R*)-6-phenyl-5,6,7,8,8a,9,10,11,12,14-decahydro[1,2-*b*][2]benzazonin-5-ol gave the ketone **17** in poor yield. A milder oxidation of the alcohol using the Cornforth reagent[5] gave the ketone in much better yield (typically 65%) although the oxidation was slow to go to completion (3 days). Comparison of the C9 and C11 ^{13}C NMR signals of the ketone to that of the alcohol **3** show these carbon atoms to be shielded by *ca.* 4ppm due to the C14/C9, C11 γ-axial effect. This effect also lowers the ^{13}C NMR chemical shift of the C14 carbon atom relative to the *trans*-fused alcohol **3** by *ca.* 4ppm. The low chemical shift of the C12 carbon atom relative to the alcohol **3** can be accounted for by the close proximity of the ketone oxygen to the C12 axial/equatorial hydrogens. The C8a proton in the ^1H NMR spectrum of the ketone was located by homonuclear decoupling. The C14 protons are located at δ3.7 and δ4.3 (J_{gem}=-15.3Hz). The small chemical shift difference between these indicate *cis*-fusion. The C6-*H* is located at δ3.9 as a doublet of doublets, *J*vic 6,7=11,3Hz. The Karplus relationship predicts dihedral angles of *ca.* 180° and *ca.*60° or 125° for the couplings of 11.48Hz and 2.55Hz respectively. Dreiding models allow the two possible orientations of the C6 phenyl group to be assessed and the estimated dihedral angles between C6 and C7 protons to be set up. The two possible orientations of the phenyl group are pseudo axial and equatorial. The pseudo axial phenyl conformer is sterically unfavourable due to interactions between the two sets of aromatic groups whereas the pseudo equatorial phenyl is sterically more comfortable and gives the dihedral angles between the C6-*H* and C7-*H* protons of *ca.* 180° and *ca.* 60° which is close in agreement to the couplings observed and predicted by the Karplus relationship. The stereochemistry of *rel*-(6S, 8aR)-6-phenyl-6,7,8,8a,9,10,11,12-decahydro[1,2-*b*][2]benzazonin-5-(6*H*)-one is thus depicted below containing a *cis*-B/C ring fusion.



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Experimental

Elemental analyses were carried out at Glaxo Group Research Limited. ^1H and ^{13}C NMR spectra were determined at 270 and 68 MHz respectively on a JEOL GS spectrometer. Mass spectra were recorded on a JEOL JMS-DX303 GC/Mass spectrometer. Column chromatography was carried out over silica. M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected.

Rel-(5S,6*S*,8a*R*)-6-*p*-*chlorophenyl*-5,6,7,8,8a,9,10,11,12,14-*decahydro*[1,2-*b*][2]*benzazonin*-5-*ol* **4** and *rel*-(5*R*,6*S*,8a*R*)-6-*p*-*chlorophenyl*-5,6,7,8,8a,9,10,11,12,14-*decahydro*[1,2-*b*][2]*benzazonin*-5-*ol* **5** *Rel*-(6*S*,8a*R*)-6-*p*-*chlorophenyl*-6,7,8,8a,9,10,11,12-*octahydropyrido*[1,2-*b*][2]*benzazonin*-5,14-*dione* **3** (0.75g, 2mmol) in tetrahydrofuran (50ml) was added to a stirred slurry of lithium aluminium hydride (0.15g) in tetrahydrofuran (25ml). The resulting mixture was heated and stirred and heated under reflux for 60h. Water was carefully added dropwise until the excess lithium aluminium hydride had been decomposed. The mixture was filtered and the solvents removed under reduced pressure. Column chromatography of the residue over silica using chloroform as the elutant gave *Rel*-(5S,6*S*,8a*R*)-6-*p*-*chlorophenyl*-5,6,7,8,8a,9,10,11,12,14-*decahydro*[1,2-*b*][2]*benzazonin*-5-*ol* **4** as a white crystalline solid. Recrystallization from petroleum ether (b.p. 40-60°C) gave **4** as a white crystalline solid 0.28g, m.p. 121.5-122°C, $\nu_{max.}$ (Nujol) 3500 and 1600 cm^{-1}, δ($CDCl_3$) 8.9 (1H, S, OH), 7.05-7.4 (8H, m, ArH), 4.7 (1H, bd, CHOH) 4.45, 3.35 (2H, AB, NCH_2Ar), 3.05 (1H, m, $NCH(CH_2)_2$), 2.15 (1H, m NCH_{ax}) and 1.2-2.8 (10H, m, aliphatic); ^{13}C-NMR (methine protons were assigned by DEPT experiments) δ: 136.4, 131.3, 129.3, 129.8, 130.1, 134.7 (C14a-C4a), 81.9 (C5), 53 (C6), 30 (C7), 23.7 (C8), 60 (C8a), 32 (C9), 25 (C10), 26.4 (C11), 53.7 (C12), 59.6 (C14), 135.1, 131.1, 132.3, 137.4, 132.8, 130 (C6-*p*-ClPh); M/e 355, 357 (M^+), 339, 337 (M^+-H_2O). (Found: C, 74.6; H, 7.4; N, 3.8. $C_{22}H_{26}NOCl$ requires C, 74.3; H, 7.3; N, 3.9%). Further elution with dichloromethane 94%, ethanol 5% and ammonia 1% (500ml) gave *rel*-(5*R*,6*S*,8a*R*)-6-*p*-*chlorophenyl*-5,6,7,8,8a,9,10,11,12,14-*decahydro*[1,2-*b*][2]*benzazonin*-5-*ol* **5** as an oil (85mg), $\nu_{max.}$ (liquid film) 3500 and 1600cm^{-1}; δ ($CDCl_3$) 6.8-7.4 (8H, m, ArH), 5.0 (1H, d, CHOH), 4.4, 4.55 (2H, AB, NCH_2Ar), 3.3 (1H, m, CH(Ph)), 2.9 (1H, m, NCH_{eq}), 2.7 (1H, m NCH_{ax}), 2.4 (1H, m, $NCH(CH_2)_2$) and 1.2-2.0 (10H, m, aliphatic; ^{13}C-NMR (methine protons were assigned by DEPT experiments) δ: 135.8, 131.4, 130.6, 132.1, 131.7, 136.8 (C14a-C4a), 74.7 (C5), 54.9 (C6), 30.7 (C7), 22.7 (C8), 56 (C8a), 29.1 (C9), 22.2 (C10), 26.8 (C11), 50.4 (C12), 63.1 (C14), 137.4, 130.9, 133, 138, 133.4, 131.6 (C6-*p*-ClPh); M/e 355, 357 (M^+), 339, 337 (M^+-H_2O). (Found: C, 73.8 H, 7.1; N, 3.6. $C_{22}H_{26}NOCl$ requires C, 74.3; H, 7.3; N, 3.9%).

Rel-(4a*R*,7*R*,7a*R*,13*R*)1,2,3,4a,5,6,7,7a12-*decahydro*-7-*phenylisoindol*-[1,2-*d*][2]*quinolizin*-13-*ium phosphate* **11** and *rel*-(5*R*,6*R*,8a*R*)-6-*phenyl*-5,6,7,8,8a,9,10,11,12,14-*decahydro*[1,2-*b*][2]*benzazonin*-5-*ol* **13.** *Rel*-(5*S*,6*S*,8a*R*)-6-phenyl-5,6,7,8,8a,9,10,11,12,14-decahydropyrido[1,2-*b*][2]benzazonin-5-ol **3** (1g, 2.8 mmol) was dissolved in ice cold pyridine (3.6ml). Phosphorus oxychloride (0.87g) was added and the mixture left in a refrigerator overnight. Saturated sodium bicarbonate (20ml) was cautiously added and the resulting solution extracted with chloroform. The combined extracts were dried (Na_2SO_4) and the solvent removed under reduced pressure to give a thick dark oil. Chromatoghraphy over Woelm neutral alumina grade IV using chloroform as the elutant gave a white crystalline solid. Recrystallization from ethylacetate/ethanol 10/1

gave *rel*-(4a*R*,7*R*,7a*R*,13*R*)1,2,3,4a,5,6,7,7a,12-*decahydro*-7-*phenylisoindol*-[1,2-*d*][2]*quinolizin*-13-*ium phosphate* **11** as a white crystalline solid (0.37g, 37%), m.p. 158-158.5°C, ν_{max} (Nujol) 1600 and 750 cm^{-1}; δ($CDCl_3$) 7.0 (8H,m, Ar), 6.2(1H, d, CHN^+), 5.61(1H, d, ArH), 5.31(1H, m, NCH_{ax}), 5.31 (1H, m, $NCH(CH_2)_2$), 4.65 (2H, AB, NCH_2Ar), 4.9 (1H, dd, CH(Ph)), 3.25 (1H, bd, NCH_{eq}) and 1.4-2.4 (10H, m, aliphatic), ^{13}C-NMR (methine protons were assigned by DEPT experiments) δ: 56.7 (C1), 26.7 (C2), 21.3 (C3), 29.1 (C4), 61.4 (C4a), 21.5 (C5), 18.1 (C6), 39.1 (C7), 84.3 (7a), 139.6 (7b), 134.7 (C8), 132.1 (C9), 131.7 (C10), 132.6 (C11), 133.7 (C11a), 62.9 (C12), 134.9, 132, 130.4, 131.2, 131.6, 132.4 (C7-Ph); M/e 303 (M^+). (Unsatisfactory microanalytical data was obtained for this product. The presence of nonstoichiometric amounts of chloride were detected by titration with silver nitrate indicating incomplete hydrolysis of the phosphorus intermediate).

A second fraction eluted with chloroform gave a colourless oil which solidified on standing. Recrystallization from ethylacetate/ethanol gave *rel*-(5*R*,6*R*,8a*R*)-6-*phenyl*-5,6,7,8,8a,9,10,11,12,14-*decahydro*[1,2-*b*][2]*benzazonin*-5-*ol* **13** as colourless needles (0.11g, 11%), m.p. 166-7°C, ν_{max} (Nujol) 3500, 1600 and 750 cm-1, δ($CDCl_3$) 7.1-7.5 (9H, m, ArH), 5.4 (1H, s, CH(OH)), 5.4, 4.8 (2H, AB, NCH_2Ar) and 0.9-2.6 (14H, m, aliphatic); ^{13}C-NMR (methine protons were asigned by DEPT experiments) δ: 135.8, 133, 130.9, 131.3, 134.1, 138 (C14a-C4a), 80.7 (C5), 34.3 (C6), 22 (C7), 22.6 (C8), 66.2 (C8a), 26.3 (C9), 16.2 (C10), 26.1 (C11), 48.7 (C12), 62.4 (C14), 134, 132.4, 130, 129.6, 131.7, 133 (C6-Ph); M/e 321 (M^+). (Found: C, 82.3; H, 8.5; N, 4.3. $C_{22}H_{27}NO$ requires C, 82.2; H, 8.4; N, 4.4%.)

Rel-(6*S*,8a*R*)-6-*phenyl*-5,6,7,8,8a,9,10,11,12-*octahydro*[1,2-*b*][2]*benzazonin*-5-(14*H*)-*one* **17**. *Rel*-(5*S*,6*S*,8a*R*)-6-phenyl-5,6,7,8,8a,9,10,11,12,14-decahydropyrido[1,2-*b*][2]benzazonin-5-ol **3** (1g, 3.1 mmol) was dissolved in acetone (20ml), dilute hydrochloric acid (10ml) added and the mixture stirred and cooled to 0°C. Jones' reagent (1.3ml) was added dropwise and the mixture left stirring for 20mins. Methanol (2ml) was then added and the resulting mixture filtered and the solvents removed under reduced pressure. Water (15ml) was added to the residue and the solution made alkaline with saturated sodium bicarbonate. The solution was extracted with chloroform and the combined extracts dried (Na_2SO_4) and the solvent removed under reduced pressure to give an orange oil. The oil was taken up in a little ether/petroleum ether (1:1) and cooled to ice temperature whereupon fluffy white needles were deposited. Recrystallization from ether/petroleum ether (1:1) gave *Rel*-(6*S*,8a*R*)-6-*phenyl*-5,6,7,8,8a,9,10,11,12-*octahydro*[1,2-*b*][2]*benzazonin*-5-(14*H*)-*one* **17** as fluffy white needles (0.42g, 42%), m.p. 95-6°C, ν_{max} (Nujol) 1680, 1600 and 750 cm^{-1}, δ ($CDCl_3$) 6.8-7.4 (9H, ArH), 3.7, 4.3 (2H, AB, NCH_2Ar), 3.9 (1H, dd, C(Ph)H), 2.87 (1H, m, $NCH(CH_2)_2$) and 1.3-2.8 (12H, m aliphatic), ^{13}C-NMR (methine protons were assigned by DEPT experiments) δ: 139, 133.7, 130.4, 131.6, 135.4, 140.8 (C14a-C4a), 196 (C5), 56.1 (C6), 28.5 (C7), 21.9 (C8), 58.6 (C8a), 29.4 (C9), 27.3 (C10), 22.6 (C11), 45.8 (C12), 56.5 (C14), 141.3, 132.4, 131.9, 130.5, 132.5, 134 (C6-Ph); m/e 319 (M^+). (Found: C, 82.8; H, 7.8; N, 4.4. $C_{22}H_{25}NO$ requires C, 82.75; H, 7.8; N, 4.4%.)

Rel-(6*S*,8a*R*)-6-*phenyl*-5,6,7,8,8a,9,10,11,12-*octahydro*[1,2-*b*][2]*benzazonin*-5-(14*H*)-*one* **17**. *Rel*-(5*S*,6*S*,8a*R*)-6-phenyl-5,6,7,8,8a,9,10,11,12,14-decahydropyrido[1,2-*b*][2]benzazonin-5-ol **3** (2g, 6.23 mmol) was dissolved in chloroform and hydrogen gas bubbled through the mixture. The chloroform was removed under reduced pressure and the resulting gum dissolved in pyridine (20ml). A solution of chromium trioxide (0.685g) in water (10ml) was carefully added dropwise into ice cold pyridine (15ml) with vigorous stirring. The solution of

rel-(5*S*,6*S*,8a*R*)-6-phenyl-5,6,7,8,8a,9,10,11,12,14-decahydropyrido[1,2-*b*][2]benzazonin-5-ol hydrochloride in pyridine was added dropwise onto this mixture with vigorous stirring and left at room temperature for three days. The solution was filtered, basified with saturated sodium carbonate and the solvents removed under reduced pressure. Water (20ml) was added and the mixture extracted with chloroform. The combined extracts were dried (Na_2SO_4) and the solvent removed under reduced pressure to give a dark oil. Chromatoghraphy over Woelm neutral alumina grade III using ether/petroleum ether (b.p. 40-60°C) (1:1) as the elutant gave *rel*-(6*S*,8a*R*)-6-*phenyl*-5,6,7,8,8a,9,10,11,12-*octahydro*[1,2-*b*][2]*benzazonin*-5-(14*H*)-*one* **17** as shining white needles (1.31g, 64%). (Spectral data were identical to those mentioned using the previous method.)

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