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# Solvolysis of N-Chloro-1,4-dihydro-1,4-iminonaphthalenes (7-Azabenzonorbornadienes); Dependence of the Rearrangement Pathway on the Configuration at Nitrogen

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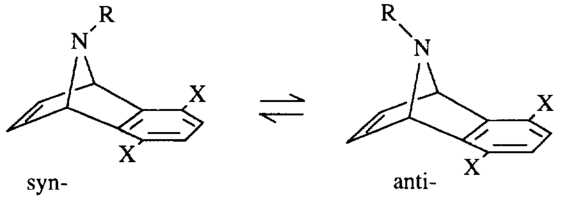
**Abstract** N-Chloro- derivatives of the 1,4-dihydro-1,4-iminonaphthalene (7-azabenzonorbornadiene) ring system undergo silver (I)-assisted rearrangement with participation of etheno- (syn-chloro- series) or benzo- (anti-chloro- series) $\pi$-electrons. The high barriers to inversion at nitrogen together with some control over the ratio of invertomers allow observation of a different reaction pathway for each invertomer when reactions are performed at low temperatures; approaches which allow selection of the benzo- participation route (giving 6,7-benzo-derivatives of the 1-azabicyclo[3.2.0]hept-3-ene ring system) are described.

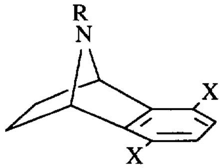
## Introduction

Attempts to link the reactivity of an amino- nitrogen to the configuration at the nitrogen atom are usually frustrated by the occurrence of rapid inversion at the nitrogen centre. This is in stark contrast to the situation in carbon chemistry where the control exerted over the reaction rate and product by the configuration of a leaving group at carbon can be taken for granted. The high inversion barriers in aziridines have allowed a considerable degree of configurational control at nitrogen[1] but the scope of reactivity studies is somewhat limited and is dominated by ring strain. Work in other azacycles has, of necessity, been performed on rapidly inverting systems. Even in strained bicyclic systems such as norbornanes, attempts to investigate direct parallels between the chemistry of *endo*- and *exo*- derivatives of the all-carbon and the 2-azanorbornyl systems were complicated by barriers which were too low to stop the inversion at nitrogen.[2] Despite this configurational mobility, work on the assisted solvolysis of N-chloroamines based on the 2-azabicyclo[2.2.1]heptyl and -[2.2.2]octyl ring systems has established that both $\sigma$- and $\pi$- participation can lead to preferential reactivity of one invertomer over the other.[3]

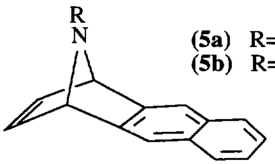
Recent investigations of configurational stability at nitrogen have centred heavily on 7-azabicyclo-[2.2.1]heptanes (7-azanorbornanes) since the inversion barriers here approach the values seen in aziridines but without the same degree of strain.[4] The first use of this ring system for solvolytic studies was by Rautenstrauch[5] who recognised the differing reactivity of the two invertomers of **(1b)** and made tentative suggestions for the structures of the reaction products. Our preliminary studies[6] led to firm structural proposals for the products from **(1b)** and extended the range of N-chloro- compounds. We have shown that a measure of control can be exerted over stereochemistry at nitrogen since N-chlorination at low temperatures can produce a heavily-biased ratio of invertomers[4b] (table 1) and may actually allow the isolation of single invertomers in some cases.[4d] The non-equilibrium ratios of invertomers can be maintained below 0°C although thermodynamic equilibrium is established at, or above, ambient temperature when rapid nitrogen inversion takes over. These studies have established a clear stereochemical foundation for reactivity studies and we now report our investigations of Ag(I)-catalysed heterolysis of the title system and of N-chloro-1,2,3,4-tetrahydro-1,4-iminonaphthalene **(3b)**, and the 1,4-dihydro-1,4-iminoanthracene analogue **(5b)**. The dimethoxybenzo- derivatives **(2b)** and **(4b)** are included here in order to reinforce structural assignments but fuller studies of the effect on the behaviour of these ring systems of substitution in the aryl ring,[7a] of replacement of the etheno- bridge with a second aryl ring,[7a] and of substitution at the bridgehead (C1, C4) positions[7b] will be reported separately.



**(1a)** X=H, R=H
**(1b)** X=H, R=Cl
**(2a)** X=OMe, R=H
**(2b)** X=OMe, R=Cl



**(3a)** X=H, R=H
**(3b)** X=H, R=Cl
**(4a)** X=OMe, R=H
**(4b)** X=OMe, R=Cl



**(5a)** R=H
**(5b)** R=Cl

**Table 1. Invertomer Ratios for N-Chloroamines formed under Kinetic and Thermodynamic Control[4b]**

| Substrate | Product | Chlorination at low temperature (Kinetic Control) syn- : anti- | After Equilibration at ambient temperature (Thermodynamic Control) syn- : anti- |
|---|---|---|---|
| **(1a)** | **(1b)** | 31 : 69 | 63 : 37 |
| **(2a)** | **(2b)** | 34 : 66 | 67 : 33 |
| **(3a)** | **(3b)** | 6 : 94 | 53 : 47 |
| **(4a)** | **(4b)** | 5 : 95 | 54 : 46 |
| **(5a)** | **(5b)** | 33 : 67 | 87 : 13 |

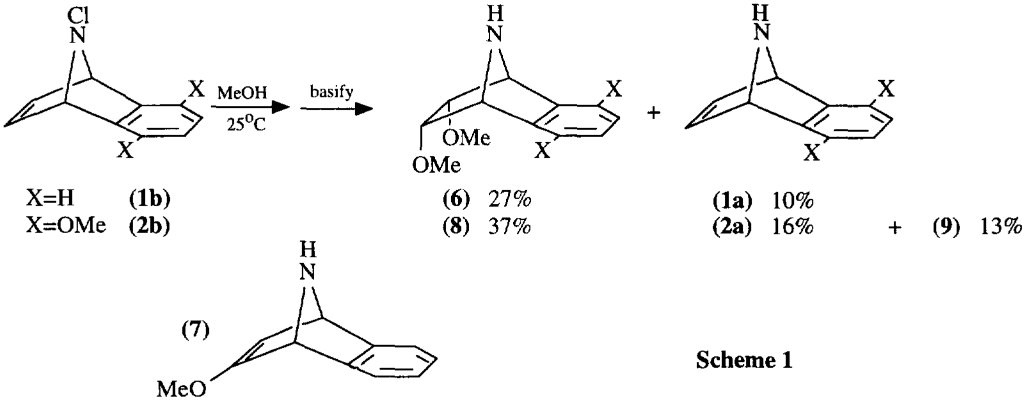
## Preparation of N-Chloroamines

Routes to the secondary amines **(1a)** - **(5a)** have already been reported[4a] as have the N-chlorination reactions leading to **(1b)** - **(5b)** including a measure of control over the N-chloroamine invertomer ratios.[4b] Thus, N-chlorination of **(1a)** - **(5a)** with N-chlorosuccinimide (NCS) in $CDCl_3$ at -50°C under conditions of kinetic control effectively prevented inversion at nitrogen in the products, preserving the initially-formed ratio of invertomers and showing a preference for the *anti-* N-chloro compound. On warming to ambient temperature, the ratio changed as the N-chloroamines began to undergo inversion until, after complete thermodynamic equilibration, the preference shifted, showing a general preference for the *syn-* invertomer.

The ratio of invertomers can thus be varied between the limits shown in table 1 simply by control of temperature. The progress of the equilibration can be monitored by $^1$H NMR spectrometry; ratios remain constant on cooling solutions to -40°C. In the case of the iminoanthracene system, a sample of *anti*-**(5b)** has been separated from a mixture of invertomers produced at 0°C by chlorination of **(5a)** using NCS in diethyl ether/dichloromethane. Evaporation of solvent followed by trituration with $CFCl_3$ at 0°C led to dissolution of the more-soluble *syn-* invertomer (together with some of the *anti-*) but left behind a solid consisting only of *anti*-**(5b)** and succinimide. This sample was kept cold and used for solvolysis studies. The isolation of a sample of **(1b)** containing only the *anti*-invertomer (by preferential solvolysis of the accompanying *syn*-N-chloro- invertomer) is described in context below.

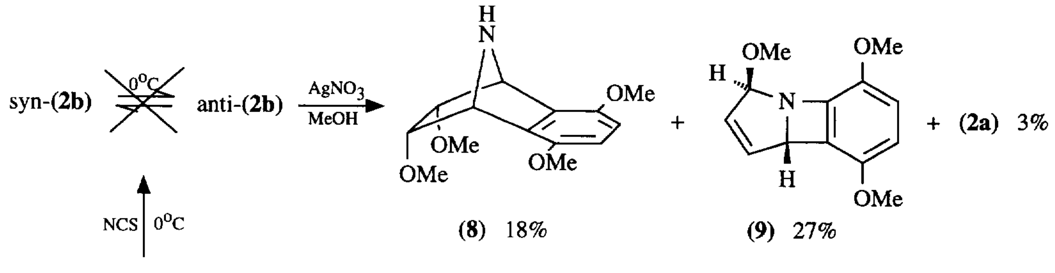
## Solvolysis Results and Discussion

A methanolic solution of the N-chloroamine **(1b)** was maintained at ambient temperature (under conditions of rapid inversion at nitrogen). All of the N-chloroamine was consumed over a period of ca. 20h and, after basification, a single methanolysis product was isolated together with some **(1a)** which presumably resulted from homolysis[8] of the N-Cl bond. The major product was assigned the structure **(6)** on the basis of the $^1$H NMR spectrum which showed a high degree of symmetry; integration confirmed the incorporation of two (equivalent) methoxy groups and the presence of a single exchangeable NH. The $^{13}$C NMR spectrum showed the expected six signals. The molecular ion was not observed in the electron-impact mass spectrum (owing to a precedented loss of the C2-C3 fragment by a retro-Diels Alder reaction[9]) but the molecular composition was confirmed by combustion analysis of the tetrafluoroborate salt. This structural assignment differed from that of Rautenstrauch[5] who had suggested the structure **(7)**.[10] We were unable to isolate any **(7)** (which could formally be obtained from **(6)** by loss of methanol). The conversion shown in Scheme 1 was confirmed by methanolysis of the dimethoxy-analogue **(2b)** under similar conditions. The analogous product **(8)** was formed from **(2b)** together with a small amount of the secondary amine **(2a)** and a third product **(9)**.



Scheme 1

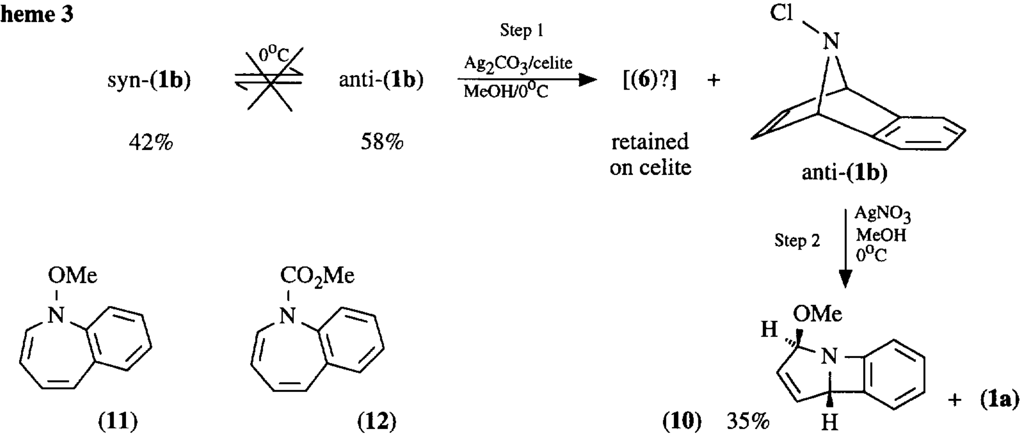
We also performed this reaction on a sample of **(2b)** prepared by chlorination at 0°C, handled at this temperature, and treated with silver nitrate in methanol at 0°C (under conditions of very slow inversion). The products are shown in scheme 2.



Scheme 2

Parallel results were obtained from the solvolysis of **(1b)** under similar conditions and a product **(10)** was isolated, corresponding closely to formation of compound **(9)** from **(2b)**. Structure **(10)** differed from the product **(11)** proposed earlier[5] but before considering structures **(9)** and **(10)** in more detail, the results from the solvolysis of **(1b)** under conditions of slow inversion will be considered. A sample of **(1b)** was prepared at 0°C in order to maximise the amount of *anti*-**(1b)**; it was shown to have equilibrated only slightly during handling, giving a *syn*- : *anti*- ratio of 42 : 58. On passage down a column of silver carbonate on Celite at 0°C, the *syn*- invertomer was completely consumed although the product [presumably **(6)**] could not be recovered from the column. The solution eluted from the column (maintained at 0°C) was shown to contain only *anti*-**(1b)** confirming the experiment of Rautenstrauch.[5] This solution was then solvolysed at 0°C in methanolic silver nitrate (scheme 3).

Scheme 3

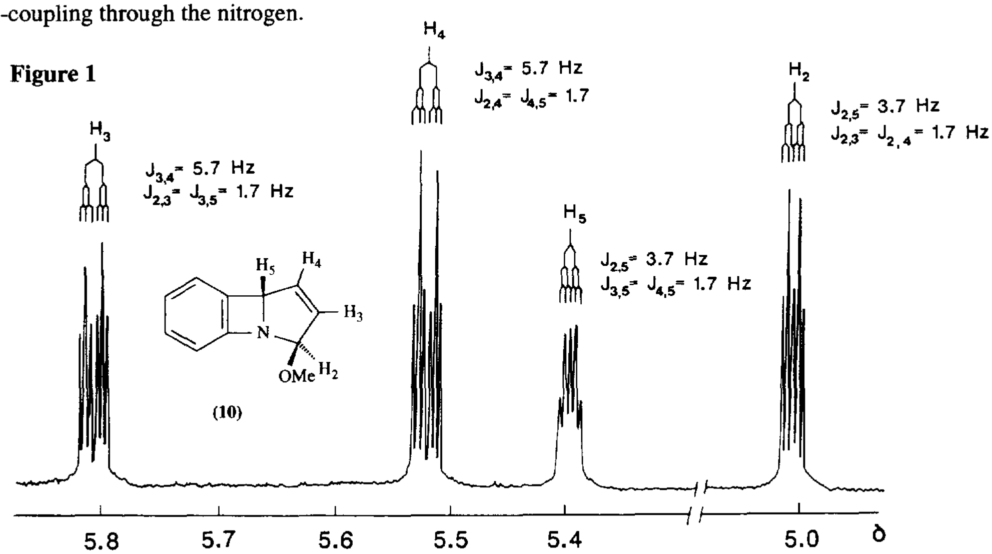


The major product was the 1-azabicyclo[3.2.0]hept-3-ene derivative **(10)** which showed a similar melting point and $^1$H NMR spectrum to those assigned to **(11)** in the earlier work. The structural revision is based on the following evidence. Both **(10)** and **(9)** were stable, crystalline solids which gave satisfactory analytical and mass spectral data. The $^{13}$C NMR spectrum of **(10)** showed only two alkenyl carbons and the aryl portion of the spectrum corresponded broadly with that of 2-ethylaniline.[11] Signals due to $H_2$ - $H_5$ in **(10)** were completely resolved in $C_6D_6$ at 400 MHz and the partial spectrum is shown in figure 1 together with J values and assignments; a similar analysis was completed for **(9)**. The assignments followed from homonuclear spin-decoupling experiments which also defined the signal at δ5.40 as the benzylic proton $H_5$ which sharpened substantially on irradiation of the aryl signal at δ7.02. The signals assigned to $H_2$ and $H_5$ showed the greatest downfield shifts on protonation of the amino- nitrogen with trifluoroethanoic acid. The $^1$H NMR and UV spectra of **(10)** bore no resemblance to the spectra reported for **(12)**,[12] a model for **(11)**. The

UV absorption maximum of **(10)** was unchanged on hydrogenation, which involved the uptake of only one mole equivalent of hydrogen and finally eliminated structure **(11)** from further consideration.

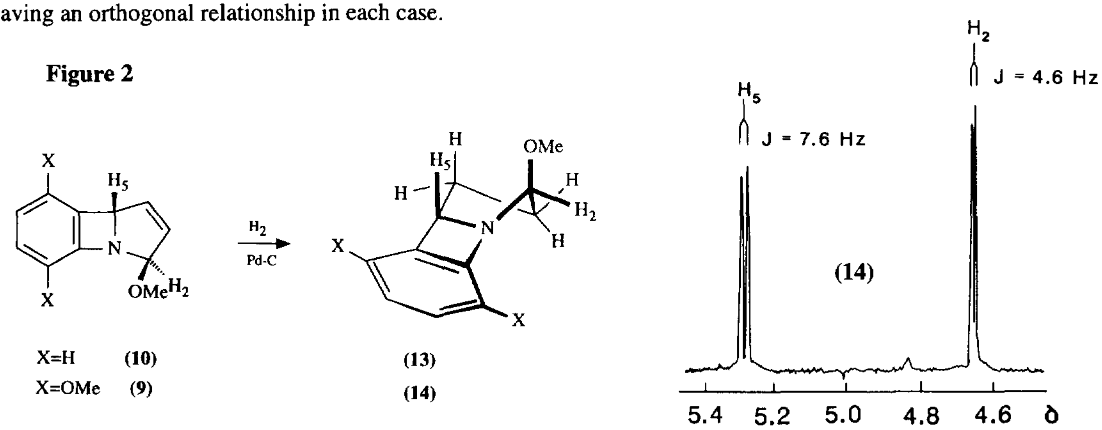
The observed value of 3.7 Hz ascribed to $J_{2,5}$ in **(10)** compared well with the value of 3.5 Hz observed for *trans*- homoallylic coupling in 1,2-fused-2,5-dihydropyrroles such as retronicine.[13] This coupling disappeared on hydrogenation of **(10)** (together with the signals due to $H_3$ and $H_4$), eliminating any suggestion of W-coupling through the nitrogen.

**Figure 1**



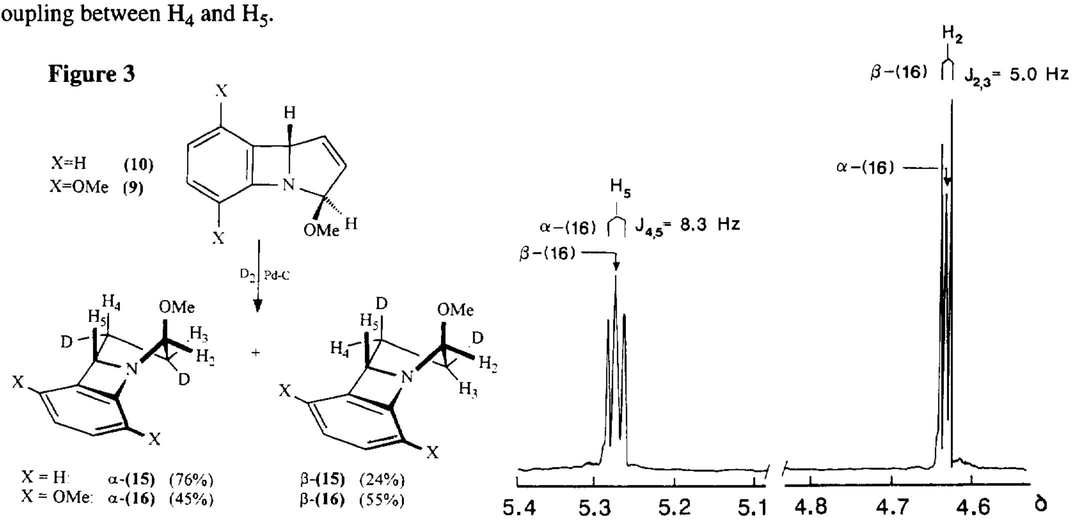
The *trans*- relationship of $H_2$ and $H_5$ was confirmed by scrutiny of the $^1H$ NMR spectra of the hydrogenated amines **(13)** and **(14)** and their deuteriated analogues **(15)** and **(16)**. Both series demonstrated similar behaviour which will be illustrated using compound **(9)**. The conformation of the pyrrolidine ring is defined by the observation (figure 2) that both $H_2$ and $H_5$ appear as doublets since this is the only shape which leads to splitting of $H_2$ and $H_5$ by only one of the neighbouring methylene protons, the second vicinal proton having an orthogonal relationship in each case.

**Figure 2**

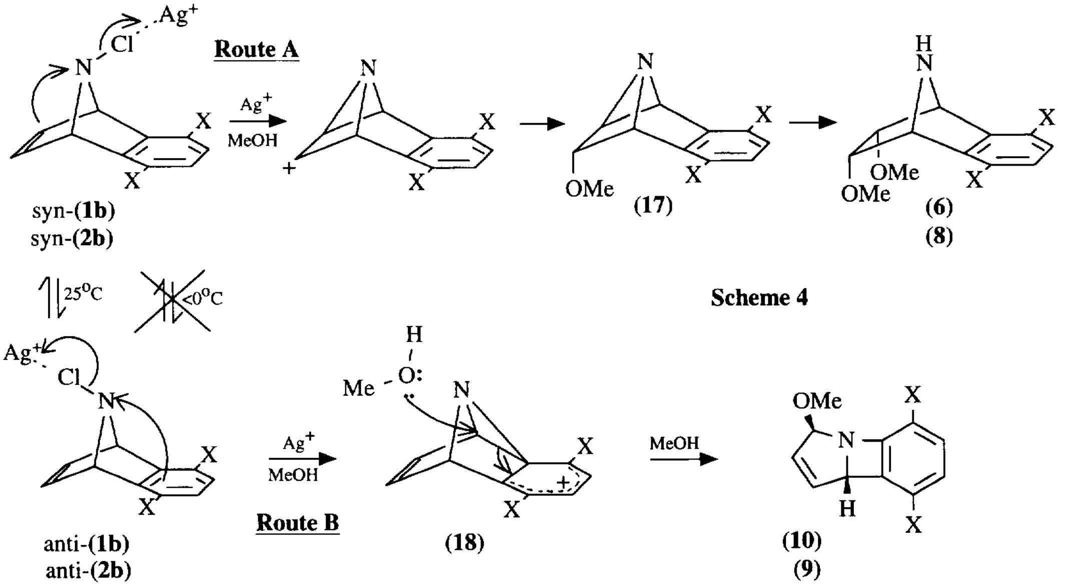


Catalytic addition of deuterium to the double bond gave an unequal mixture of products (α-**(16)** and β-**(16)** = 45:55) by attack from the two faces (the corresponding ratio of α-**(15)** and β-**(15)** from addition of deuterium to **(10)** was 76:24). Examination of the integrals allowed identification of the signals due to the α- and β- isomers. It was clear that α-**(16)** showed a doublet and a singlet respectively for $H_5$ and $H_2$ whilst β-**(16)** showed a corresponding singlet and doublet, overlapping as shown in figure 3. Addition of $D_2$ to the α- face of (9) thus leaves substantial coupling between $H_4$ and $H_5$ in α- (16) but no significant interaction between $H_2$ and $H_3$ which are seen to be close to orthogonal. The reverse situation results from addition of $D_2$ to the β- face of (9) with a substantial, but smaller, interaction between $H_2$ and $H_3$ in β-(16) and zero coupling between $H_4$ and $H_5$.

**Figure 3**



The participation of etheno- π-electrons in the loss of the chloride ion from *syn*-(**1b**) and (**2b**) and participation of the benzo- π-electrons in loss from *anti*-(**1b**) and (**2b**) is thus confirmed but the product of each of the rearrangement paths differs from that originally proposed.[5] It is apparent that the configuration at nitrogen exerts total control over the rearrangement pathway.

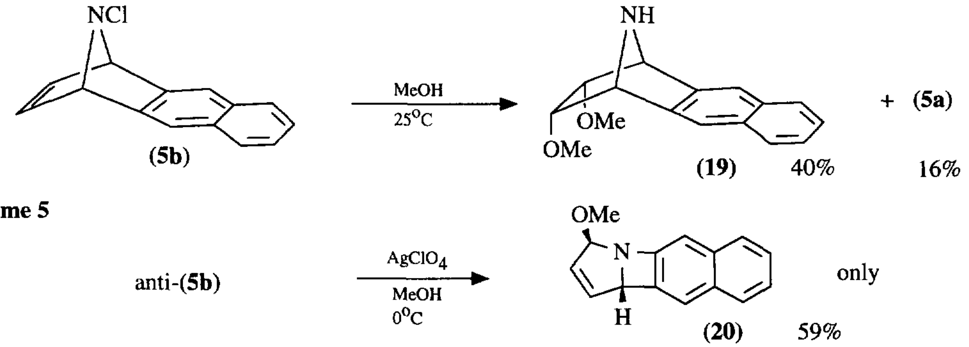


**Scheme 4**

Thus, at ambient temperature, or above, the product (**6**) obtained from (**1b**) is derived from the *syn*-chloro invertomer; the less-reactive *anti*- invertomer reacts by prior inversion to the *syn*-. In the case of (**2b**) the picture is closely similar, giving (**8**) as the main product, but the methoxy substituents endow the aryl ring with a greater ability to participate allowing some competition from direct reaction of *anti*-(**2b**) to yield a small percentage of (**9**). A clean distinction between the two separate pathways is apparent when the reactions are performed at low temperature when inversion at nitrogen is prevented[4a,b] and a direct connection between substrates and products becomes possible. The mechanism is summarised in scheme 4. The intermediate cations are pictured as localised carbocation structures for clarity but it is likely that symmetrical, non-classical intermediates are involved in these symmetrical systems.

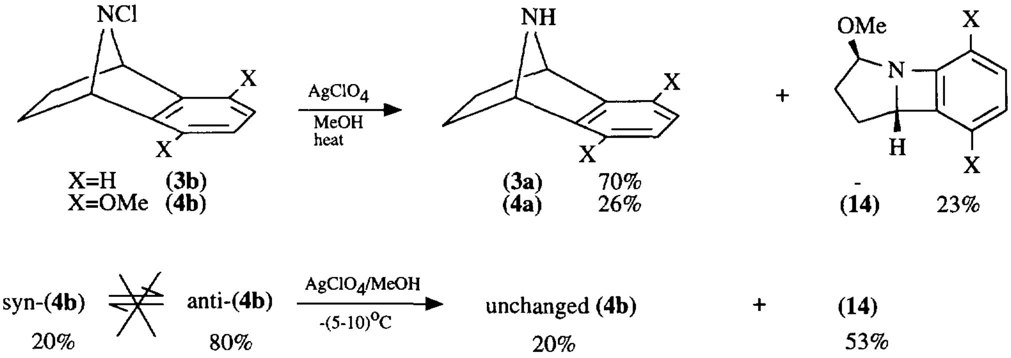
Clearly, route A can be encouraged simply by raising the temperature so that inversion becomes rapid relative to the rate of heterolysis, minimising any reaction *via* the *syn-* invertomer (route B). The products from route B are available without any intrusion from route A only if the pure *anti*-chloroamine can be isolated or if the etheno-participation route is suppressed. Examples of both of these approaches are illustrated by studies of (**3b**), (**4b**) and (**5b**) summarised in schemes 5 and 6. Taking the iminoanthracene (**5b**) first, methanolysis at ambient temperature followed the pattern observed earlier, and gave (**19**) as the only rearrangement product, contaminated with some (**5a**). However, dissolution of pure, crystalline *anti*-(**5b**) in methanol at 0°C followed by stirring with silver perchlorate[14] provided (**20**) as the sole isolated product in 59% yield. The structures of (**19**) and (**20**) followed straightforwardly from comparison of $^1$H NMR and other spectra with those for compounds (**6**) and (**10**).

**Scheme 5**



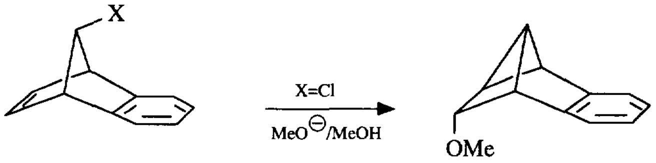
The N-chloroamines (**3b**) and (**4b**) do not have the option of etheno-participation (route A). When a solution of (**3b**) in methanol was warmed to 40°C in the dark in the presence of silver perchlorate, the major product was the secondary amine (**3a**),[15] suggesting that the reactivity of the ethano- bridged systems was reduced and/or that homolytic cleavage of the N-Cl bond was easier in this case. However, the effect of the methoxy- substituents in increasing the participatory ability of the aryl ring was again illustrated by reaction of (**4b**). Thus, when (**4b**) was methanolysed under similar conditions, the rearranged product (**14**) was formed in competition with the secondary amine (**4a**) (scheme 6).

**Scheme 6**



The situation here was confirmed when a sample of **(4b)**, which had been formed under conditions of kinetic control but had partly equilibrated, was methanolysed at low temperature in the presence of Ag(I) (scheme 6). The *anti*-**(4b)** (80% of the mixture) solvolysed to provide an isolated yield of 53% of **(14)**; the *syn*-**(4b)** (20%) did not react and was re-isolated without loss after the reaction (but as a *syn-/anti-* mixture having been allowed to invert at ambient temperature during the work-up procedure and subsequent chromatography).

The proposed mechanisms are analogous to those established in studies of closely related carbon compounds. Selected examples are shown in scheme 7. Thus, it has long been established,[16] that π-participation by the electrons of the etheno- bridge in the *syn*-chloro- compound **(21a)** led to formation of the *endo*-methoxy derivative **(22)** together with **(21b)** formed with retention of configuration.

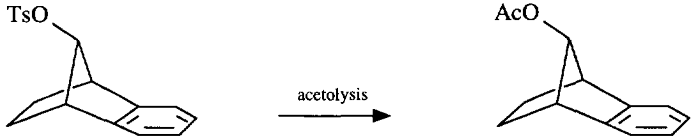


**(21a)** X=Cl
**(21b)** X=OMe

**(22)**

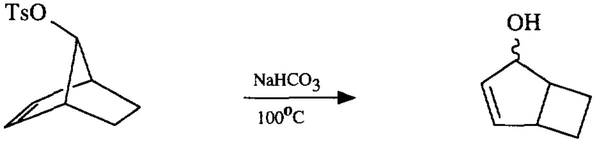
The tricyclo[4.1.0.0$^{4,7}$]heptane derivative **(22)** provides an exact parallel with the proposed intermediate **(17)** (scheme 4) but the ring-opening of the strained nitrogen analogue **(17)** in methanol in the presence of acid is unavoidable. Aryl participation with retention of configuration has been established by Tanida and others[17] and is illustrated by the acetolysis of **(23)** which produces **(24)**. We do not observe products of retained structure by nucleophilic attack at the nitrogen in either route A or B. This is not surprising in view of the established tendency of incipient nitrenium ions to undergo rearrangement, placing positive charge on carbon.[3] The attack of the nucleophile at the carbon centre in **(18)** (scheme 4) is to be expected although the production of the 1-azabicyclo[3.2.0]heptane ring system in **(9)** and **(10)** is closer in overall outcome to the 1,2-rearrangements established by Winstein[18] in conversions such as **(25)** → **(26)**. The 1,2- rearrangement of the aryl carbon in the conversion of **(1b)**, **(2b)** and **(5b)** into **(10)**, **(9)** and **(20)** respectively is thus a novel observation. However, it effectively constitutes an electrophilic aromatic substitution process, overall.

**(23)**



**(24)**

**(25)**



**(26)**

In summary, close parallels are to be found between the solvolysis of these bridged nitrogen compounds and well-studied carbon analogues. Control over reaction pathways and products by leaving group stereochemistry is a pivotal feature of the chemistry of carbon compounds. This work shows that the same principles apply to the chemistry of analogous nitrogen compounds and, given appropriate barriers to inversion at nitrogen, can be used to exert a significant degree of control over the course of reactions. Our investigations into the effects of a wider range of substituents in the aryl ring and at the 1- and 4- positions of the 7-azabicyclo[2.2.1]heptenyl system will be reported separately.[7]

## Experimental

Routine $^1$H NMR spectra were recorded on Varian EM 390 (90 MHz) or Jeol JNM-PS100 (100 MHz) spectrometers and low field $^{13}$C NMR spectra on a Jeol JNM FX60 spectrometer operating at 15.4 MHz. Higher field $^1$H and $^{13}$C NMR spectra were recorded on a Brucker ARX 250 MHz spectrometer; some spectra were obtained at 400/100 MHz by the SERC High-Field NMR Service at the University of Warwick. Spectra were measured in $CDCl_3$ with tetramethylsilane (TMS) as internal reference unless indicated otherwise. Signal characteristics are described using standard abbreviations: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiplet), br (broad); protons identified as NH or OH were shown to be exchangeable with $D_2O$. In the $^{13}$C NMR spectra, C, CH, $CH_2$, $CH_3$ are used, where appropriate, to indicate quaternary, methine, methylene and methyl carbons respectively, as shown by off-resonance decoupling or DEPT experiments.

IR spectra were recorded on PE 1604 FT or PE 298 IR spectrometers as solutions in $CH_2Cl_2$ unless indicated otherwise. Band intensities are described using standard abbreviations: s (strong), m (medium), w (weak), br (broad), v (very).

UV spectra were measured using a Pye-Unicam SP900 spectrometer.

Mass spectra were measured routinely on a VG Micromass 14 spectrometer and were obtained using ionisation by electron impact; the base peak is indicated by an asterisk. Accurate mass measurements were obtained through the SERC service at University College Swansea.

Melting point measurements were made using a Kofler hot stage apparatus and are uncorrected.

Combustion Analyses were performed by CHN Analysis Ltd. of South Wigston, Leicester.

Reactions were performed under dry nitrogen using solvents dried by standard methods. Diethyl ether was dried over sodium wire and distilled from $LiAlH_4$. Dichloromethane and methanol were distilled from calcium hydride. Petroleum ether and ethyl ethanoate were distilled prior to use. Thin-layer chromatography (TLC) was conducted on standard commercial aluminium sheets pre-coated with a 0.2 mm layer of silica gel (Merck 60 - 254).

### 9-Chloro-1,4-dihydro- and 1,2,3,4-tetrahydronaphthalen-1,4-imines (1b) and (2b)

**General procedure** (See also reference 4b for methods and full spectroscopic data.)

The secondary amine (2 - 3 mmol) was dissolved in dry diethyl ether (10 ml) and cooled to 0°C. N-Chlorosuccinimide (1.1 molar equivalents) was added in one portion and the mixture stirred rapidly in the dark under dry $N_2$ for 2h. The solvent was removed under vacuum whilst the flask was immersed in ice-water and the residue was then extracted with cold $CFCl_3$ (5 x 5 ml). The combined organic extracts were dried, filtered and the solvent removed at 0°C to produce the N-chloroamines. The N-chloro-1,4-dihydronaphthalen-1,4-imines were light-sensitive and were stored in the dark at -40°C. Each N-chloroamine was prepared only as required in order to avoid decomposition on storage.

### Methanolysis of 9-chloro-1,4-dihydronapthalen-1,4-imines (1b) and (2b) at ambient temperature

**General procedure**

The N-chloroamines (0.7 - 1.6 mmol) were dissolved in a minimum of dry methanol (5 - 10 ml) and allowed to stand at ambient temperature in the dark under dry $N_2$. The progress of each reaction was monitored by $^1$H nmr spectroscopy. After completion, the solvent was evaporated and the residue taken into $CH_2Cl_2$ and then treated with 0.1M $K_2CO_3$ solution. The aqueous phase was washed further with portions of dichloromethane and the combined organic extracts were dried and concentrated under vacuum.

The products from the solvolysis were separated by thick-layer chromatography using alumina plates and 1:1 dichloromethane:ethyl ethanoate as solvent.

**Methanolysis of (1b)**

The principal product from the solvolysis of **(1b)** at ambient temperature was the amine **(6)** which was purified by bulb-to-bulb distillation and isolated in 27% yield. $\delta_H$ ($CDCl_3$): 7.40 - 7.0 (m, 4H, Ar), 4.50 (m, 2H, $w_{\frac{1}{2}}$ = 6 Hz, $H_{1,4}$), 4.03 (m, 2H, $w_{\frac{1}{2}}$ = 6 Hz, $H_{2,3}$), 3.28 (s, 6H, OMe), 2.46 (br, s, NH). (dt, 1H, $J_{2,5}$ = 3.7, $J_{2,3}$ = 1.7, $J_{2,4}$ = 1.7 Hz, $H_2$), 3.38 (s, 3H, OMe). $\delta_C$ ($CDCl_3$, 62.5 MHz): 143.7 ($C_{9,10}$), 125.7 ($C_{5,8}$), 121.0 ($C_{6,7}$), 76.6 ($C_{1,4}$), 62.6 ($C_{2,3}$), 56.9 ($OCH_3$). $\nu_{max}$ ($CH_2Cl_2$): 3300w, 2980s, 2920s, 2820s, 1455s, 1350m, 1200s, 1145s, 1110s, 1070s, 1030s, 995s, 885s, 850s, 790s $cm^{-1}$. $^m/z$ 206 (M + 1), 190, 174,* 158, 142, 118. The amine **(6)** was analysed as the tetrafluoroborate salt which sublimed above 275°C. Found: C, 48.75; H, 5.57; N, 4.79%. $C_{12}H_{16}NBF_4O_2$ requires C, 49.18; H, 5.50; N, 4.78%. The dechlorinated compound **(1a)** was also isolated in 10% yield. The yields of **(6)** and **(1a)** present in the crude reaction mixture prior to chromatography were estimated to be 32% and 11% respectively by integration of the $^1H$ NMR signals relative to a known weight of p-dibromobenzene as internal standard (±3%).

### Methanolysis of (2b)

Treatment of **(2b)** under similar conditions led, after chromatographic separation, to the isolation of 5,8-dimethoxy-2,3-bis-*endo*-methoxy-1,2,3,4-tetrahydronapthalen-1,4-imine **(8)** (37%), 5,8-dimethoxy-1,4-dihydronapthalen-1,4-imine **(2a)** (16%), and 2-methoxy-6,7-(1,4-dimethoxybenzo)-1-azabicyclo[3.2.0]hept-3-ene **(9)** (13%). Spectroscopic and other data for these compounds are given below. An estimate of the yields before chromatography was made by direct integration of the $^1H$ NMR spectrum of the crude reaction product (using a known weight of propanone as an internal standard) and gave values of 47% : 25% : 11% (±3%) respectively for **(8)**, **(2a)**, and **(9)**.

### Ag(I)-Promoted methanolysis of 9-chloro-1,4-dihydronaphthalen-1,4-imine (1b) at 0°C

A sample of the N-chloroamine **(1b)** was prepared at low temperature and shown by $^1H$ NMR spectroscopy to consist of a mixture of *syn*- and *anti*- invertomers in a 42 : 58 ratio. This sample (718 mg, 4 mmol) was dissolved in a minimum of ice-cold methanol and placed onto a 15 cm chromatography column packed with silver carbonate-Celite[19] in dry methanol and maintained at 0°C. The column was allowed to stand for 25 min at 0°C in a cold-room and then the column was thoroughly eluted with further cold methanol. The solvent was removed under vacuum in the cold and the $^1H$ nmr spectrum of the product showed the presence of anti-**(1b)** only.

The anti-invertomer was dissolved in 5 ml of ice-cold methanol and added to a rapidly stirred solution of silver nitrate (1.0 g) in methanol (15 ml) at 0°C. The mixture was stirred in an ice-water bath for 15 min after which time it was filtered and extracted with petroleum ether (4 x 20 ml). The organic extracts were combined, dried and the solvent removed under vacuum to give 2-methoxy-6,7-benzo-1-azabicyclo(3.2.0)-hept-3-ene **(10)** (140 mg). The methanol layer was evaporated under vacuum and the residue extracted with dichloromethane to yield an oil (365 mg) which was chromatographed on basic alumina using 1:1 petroleum ether:diethyl ether as eluant to give an additional sample of pure **(10)** (102 mg). The total yield was 242 mg (34 %). The solid was recrystallised several times from petroleum ether, m.p. 61 - 62.5°C (lit.[5] 61 - 62°C). $\delta_H$ 400 MHz ($C_6D_6$): 7.12 (m, 1H, Ar), 6.78 (d, 2H, Ar), 6.63 (d, 1H, Ar), 5.81 (dt, 1H, $J_{3,4}$ = 5.7, $J_{2,3}$ = 1.7, $J_{3,5}$ = 1.7 Hz, $H_3$), 5.52 (dt, 1H, $J_{2,4}$ = 5.7, $J_{3,4}$ = 1.7, $J_{4,5}$ = 1.7 Hz, $H_4$), 5.40 (dt, 1H, $H_{2,5}$ = 3.7, $J_{3,5}$ = 1.7, $J_{4,5}$ = 1.7 Hz, $H_5$; broadened slightly by coupling to the o-aryl proton), 5.00 (dt, 1H, $J_{2,5}$ = 3.7, $J_{2,3}$ = 1.7, $J_{2,4}$ = 1.7 Hz, $H_2$), 3.38 (s, 3H, OMe). $\delta_C$ ($CDCl_3$): 157.6 (aryl C-N), 140.0 (alkene $C_3$), 133.4 (alkene $C_4$), 128.6, 128.0 (aryl CH), 121.9 (aryl C), 120.6, 112.2 (aryl CH), 98.8 ($C_2$), 81.7 ($C_5$) 53.5 ($OCH_3$). $\nu_{max}$ ($CH_2Cl_2$): 2930w, 2820w, 1590s, 1450s, 1355s, 1185s, 1105s, 1085s, 1040s, 985s, 805w $cm^{-1}$. $^m/z$: 173 ($M^+$), 158, 141*, 114, 88. $\lambda_{max}$(cyclohexane) nm ($\epsilon$): 215 (4974), 232 (6488), 284 (2919). Found: C, 76.15; H, 6.49; N, 8.09%. $C_{11}H_{11}NO$ requires: C, 76.28; H, 6.40: N, 8.09%.

### Ag(I)-Promoted methanolysis of 9-chloro-5,8-dimethoxy-1,4-dihydronaphthalen-1,4-imine (2b) at 0°C

The N-chloroamine **(2b)** (606 mg, 2.5 mmol) was dissolved in ice-cold, dry methanol (15 ml) and added to an ice-cold solution of silver nitrate (800 mg) in methanol. The heterogeneous mixture was stirred at 0°C for 30 min. in the dark under dry $N_2$. The mixture was poured into water and 2M NaOH (20 ml) added. The basified aqueous layer was extracted with dichloromethane (4 x 25 ml) and the combined organic extracts were dried and concentrated under vacuum to give a brown oil (550 mg) which was adsorbed onto basic alumina (2.0 g). This was placed on top of a column of alumina which was then eluted with diethyl ether. This gave firstly, 2-methoxy-6,7-(1,4-dimethoxybenzo)-1-azabicyclo(3.2.0)hept-3-ene **(9)**, m.p. 64.5 - 67°C (159 mg, 27%). $\delta_H$ ($CDCl_3$, 400 MHz): 6.68 and 6.40 (dd, 2H, AB system, $J_{AB}$ = 9 Hz, Ar), 6.38 (dt, 1H, $J_{3,4}$ = 5.7, $J_{2,3}$ = 1.7, $J_{3,4}$ = 1.7 Hz, $H_3$), 5.80 (dt, 1H, $J_{3,4}$ = 5.7, $J_{2,4}$ = 1.7, $J_{4,5}$ =1.7 Hz, $H_4$), 5.79 (dt, 1H, $J_{2,5}$ = 3.5, $J_{3,5}$ = 1.7, $J_{4,5}$ = 1.7 Hz, $H_5$; broadened slightly by coupling to the o-aryl proton), 5.31 (dt, 1H, $J_{2,5}$= 3.5, $J_{2,3}$ = 1.7, $J_{2,4}$ = 1.7 Hz, $H_2$), 3.82 and 3.80 (2 x s, total 6H, ArOMe), 3.55 (s, 3H, OMe). $\delta_C$ ($CDCl_3$, 62.5 MHz): 147.8, 144.3, 141.7 (3 x aryl C), 134.0, 129.8 (2 x CH), 124.9 (aryl C), 114.4, 110.2 (2 x CH), 97.2 ($C_2$), 81.1 ($C_5$), 57.1 & 56.9 (2 x $ArOCH_3$), 54.6 ($OCH_3$). $\nu_{max}$ ($CH_2Cl_2$): 2940m, 2830w, 1580m, 1485s, 1425s, 1325m, 1230s, 1105s, 1075s, 1015s, 980s, 845s $cm^{-1}$. $^{m}/z$: 233($M^+$), 218, 202*, 190, 174, 160. $\lambda_{max}$ (cyclohexane) nm ($\epsilon$): 217.5 (13431), 237 (6567), 290 (3134). Found: C, 66.87; H, 6.49; N, 5.98%. $C_{13}H_{15}NO_3$ requires: C 66.94; H, 6.48; N, 6.00%. Further elution with diethyl ether gave 2,3-*endo*-dimethoxy-5,8-dimethoxy-1,2,3,4-tetrahydronapthalen-1,4-imine **(8)** m.p. 154 - 156°C (122 mg, 18%). $\delta$ ($CDCl_3$): 6.62 (s, 2H, Ar), 4.78 (m, 2H, $w_{\frac{1}{2}}$ = 5 Hz, $H_{1,4}$), 4.08 (m, 2H, $w_{\frac{1}{2}}$ = 5 Hz, $H_{2,3}$), 3.75 (s, 6H, ArOMe), 3.42 (s, 6H, OMe), 2.06 (br, s, NH, exchangeable with $D_2O$). $\delta_C$ ($CDCl_3$, 62.5 MHz): 149.6 ($C_{5,8}$), 134.6 ($C_{9,10}$), 110.8 ($C_{6,7}$), 78.1 ($C_{1,4}$), 61.7 ($C_{2,3}$), 58.7 ($ArOCH_3$), 56.1 ($OCH_3$). $\nu_{max}$ ($CH_2Cl_2$): 3290w, 2990m, 2830m, 1633w, 1495s, 1300m, 1245m, 1200m, 1085m, 995m, 795s $cm^{-1}$. $^{m}/z$: 265 ($M^+$), 234, 177*, 162, 147, 134, 119. Found: C, 63.04; H, 7.08; N, 5.43%. $C_{14}H_{17}NO_4$ requires: C, 63.38; H, 7.22; N, 5.28%. The column was stripped with methanol and, from this residue, 5,8-dimethoxy-1,4,dihydronapthalen-1,4-imine **(2a)** was isolated by column chromatography followed by preparative thick-layer chromatography. The total yield of material was 20 mg (3%) which had an identical $^1H$ nmr spectrum to that of authentic **(2a)**.

### Hydrogenation of 2-methoxy-6,7-benzo-1-azabicyclo[3.2.0]hept-3-ene derivatives (9) and (10)

### General method

The amine **(9)** or **(10)** (10 - 20 mg) was dissolved in diethyl ether (10 ml) and 0.5 - 1 mg of Pd-C catalyst added. The heterogeneous mixture was stirred in a 25 ml r.b. flask which was flushed with dry $N_2$ for *ca.* 10 minutes. The system was then evacuated (water pump), and hydrogen (or deuterium) gas admitted from a balloon. The reaction mixture was stirred overnight after which time the catalyst was filtered off through a pad of Celite and the filter cake washed copiously with diethyl ether. The solution was dried and evaporated under vacuum to yield the product in quantitative yield.

Hydrogenation of **(10)** gave **(13)**: $\delta_H$ ($CDCl_3$, 90 MHz): 7.28 - 6.87 (m, 3H, Ar), 6.82 (d, 1H, Ar), 5.2 (m, $H_5$), 4.43 (m, $H_2$), 3.43 (s, 3H, OMe), 2.13 - 1.83 (m, 4H, $H_{3,4}$). $\nu_{max}$: 2930s, 1720w, 1585m, 1445s, 1375m, 1350m, 1185s, 1075s, 1035s, 985m, 930m, 800m $cm^{-1}$. $^{m}/z$: 175 ($M^+$), 160, 143*, 132, 115. $\lambda_{max}$ nm ($\epsilon$): 218 (4613), 233 (5250), 285 (2227).

Hydrogenation of **(9)** afforded **(14)**: m.p. 67 - 69°C. Found: C, 66.27; H, 7.25; N, 5.97%. $C_{13}H_{17}NO_3$ requires: C, 66.36; H, 7.28; N 5.95%. $\delta_H$ ($CDCl_3$, 90 MHz): 6.65 and 6.40 (AB system, J = 9 Hz, 2H, Ar), 5.28 (d, J = 7.6 Hz, $H_5$), 4.64 (d, J = 4.6 Hz, $H_2$), 3.80 (s, 3H, ArOMe), 3.78 (s, 3H, ArOMe), 3.49 (s, 3H, OMe), 2.18 - 1.93 (m, 4H, $H_{3,4}$). $\nu_{max}$: 2950s, 2830w, 1585m, 1495s, 1430m, 1245s, 1160m, 1075s, 1030m, 790m $cm^{-1}$. $^{m}/z$: 235* ($M^+$), 220, 204, 188, 174, 162, 145, 130. $\lambda_{max}$ nm ($\epsilon$): 221 (9214), 239 (5837), 291 (2571).

Addition of $D_2$ to **(10)** yielded **(15)**: $\delta_H$ ($CDCl_3$, 400 MHz): 7.18 - 6.92 (m, 3H, Ar), 6.66 (d, 1H, Ar), 5.23 ($H_5$: s for β-**(15)**, and d, $J_{4,5}$ = 8.3 Hz for α-**(15)**), 4.47 ($H_2$: d, $J_{2,3}$ = 4.6 Hz for β-**(15)** and s for α-**(15)**), 3.48 (s, 3H), 2.16 - 1.89 (m, 2H); ratio of α-**(15)** : β-**(15)** = 76 : 24. $^{m}/z$: 177 ($M^+$), 162, 144*, 134, 117, 104 (ms revealed ≥ 99% incorporation of $D_2$).

Addition of $D_2$ to **(9)** gave **(16)**: $\delta_H$ ($CDCl_3$, 400 MHz): 6.64 and 6.40 (AB system, J = 9 Hz, 2H, Ar), 5.27 ($H_5$: s for β-**(16)**, and d, $J_{4,5}$ = 8.3 Hz for α-**(16)**), 4.63 ($H_2$: d, $J_{2,3}$ = 5.0 Hz for β-**(16)** and s for α-**(16)**), 3.8 (s, 3H, ArOMe), 3.78 (s, 3H, ArOMe), 3.48 (s, 3H, OMe), 2.14 - 1.92 (m, 2H); ratio of α-**(16)** β-**(16)** = 45 : 55. $^{m}/z$: 237* ($M^+$), 222, 206, 190, 175, 162, 147, 132, 119, 94 (ms revealed ≥ 99% incorporation of $D_2$).

### Methanolysis of 11-chloro-1,4-dihydroanthracen-1,4-imine (5b) at ambient temperature

The amine **(5a)** (31 mg, 0.16 mmol) was treated with NCS (30 mg, 0.22 mmol) in $CDCl_3$ at -50°C. The consumption of starting material at this temperature was followed by $^1H$ nmr spectroscopy[4b] and, when chlorination was complete, the solvent was removed under vacuum. The residue was dissolved in a minimum of dry methanol (~1 ml) and allowed to stand at room temperature for three days. The solution was washed with 2M NaOH (2 ml) and the aqueous layer extracted with dichloromethane. The combined organic extracts were dried and the solvent removed under vacuum. Preparative thick-layer chromatography (alumina, 1:1 dichloromethane:ethyl acetate) gave the dechlorinated amine **(5a)** (5 mg, 16%) and 2,3-*endo*-dimethoxy-1,2,3,4-tetrahydroanthracen-1,4-imine **(19)** (16 mg, 40%). $\delta_H$ ($CDCl_3$): 7.85 - 7.55 (m, 4H, Ar), 7.50 - 7.28 (m, 2H, Ar), 4.66 (m, 2H, $w_{\frac{1}{2}}$ = 6Hz, $H_{1,4}$), 4.13 (m, 2H, $w_{\frac{1}{2}}$ = 6 Hz, $H_{2,3}$), 3.36 (s, 6H, OMe), 2.33 (br, s, NH). $\nu_{max}$ ($CH_2Cl_2$): 3300w, 2980m, 2930m, 2830m, 1500m, 1450w, 1350m, 1310m, 1195m, 1140s, 1105s, 1070m, 1025s, 990s, 875m, 790s $cm^{-1}$.

### Isolation of anti-11-chloro-1,4-dihydroanthracen-1,4-imine [anti-(5b)]; Ag(I)-promoted methanolysis of anti-(5b) at 0°C.

The amine **(5a)** (408 mg, 2.1 mmol) was stirred at 0°C in 1:1 diethyl ether:dichloromethane with NCS (350 mg, 2.6 mmol) for *ca.* 2h. In attempting to extract the N-chloroamine into $CFCl_3$ (*ca.* 30 ml), it was found that the syn- and anti-invertomers were partially separated, because the syn-invertomers were partially separated (syn-invertomer was considerably more soluble than the anti-invertomer). The organic extracts were combined and evaporated to give an orange solid (275 mg) which consisted of syn- and anti-**(5b)** in the ratio 67:32 ($^1H$ NMR) [$^m/z$ 227, 229 ($M^+$, 3:1)]. The residue (216 mg) consisted of pure anti-**(5b)** (together with the by-product succinimide) as shown by $^1H$ nmr spectroscopy. Integration indicated the presence of *ca.* 60 mg of pure anti-**(5b)** in the mixture.

This residue was dissolved in ice-cold methanol (10 ml) and stirred with $AgClO_4$ (123 mg) under dry $N_2$ in the dark for 1h. After this time, the mixture was filtered and evaporated and the residual brown oil taken into 0.1M $K_2CO_3$ solution (50 ml) and extracted with dichloromethane (6 x 10 ml). The combined organic extracts were washed with water (50 ml) and then dried, filtered and evaporated under vacuum leaving a brown oil (62 mg). This was adsorbed onto basic alumina which was placed on top of a pre-packed column of alumina (3.0 g). The column was eluted with 1:1 petroleum ether:diethyl ether (1:1) and the first seven fractions were combined on the basis of TLC analysis to give 2-methoxy-6,7-(2,3-naphtho)-1-aza-bicyclo-[3.2.0]hept-3-ene **(20)** m.p. 112 - 113°C (38 mg, *ca.* 59%). $\delta_H$ ($CDCl_3$, 400 MHz): 7.77 - 7.17 (m, 6H, Ar), 6.45 (dt, 1H, $H_{3,4}$ = 5.7, $J_{2,3}$ = $J_{3,5}$ = 1.7 Hz, $H_3$), 5.90 (ddt, 1H, $J_{2,5}$ = 3.6, $J_{4,5}$ = $J_{3,5}$ = 1.7, $J_{5,o\text{-}aryl}$ = 0.9 Hz, $H_5$), 5.82 (dt, 1H, $J_{3,4}$ = 5.7, $J_{2,4}$ = $J_{4,5}$ = 1.7 Hz, $H_4$), 5.25 (dt, 1H, $J_{2,5}$ = 3.6, $J_{2,4}$ = $J_{2,3}$ = 1.7 Hz, $H_2$), 3,57 (s, 3H, OMe). $\delta_C$ ($CDCl_3$, 62.5 MHz): 154.9, 138.2, 133.8 (3 x aryl C), 132.3 (CH), 129.7, (aryl C), 128.1, 127.4, 126.5, 124.5, 122.8, 118.4, 106.8 (7 x CH), 99.2 ($C_2$), 80.2 ($C_5$), 53.2 ($OCH_3$). $\nu_{max}$ ($CH_2Cl_2$): 3040w, 2920w, 2810w, 1625w, 1605w, 1415m, 1350w, 1300w, 1185m, 1145m, 1100s, 1085s, 1075s, 1035m, 980m, 855m, 800w, $cm^{-1}$; $C_{15}H_{13}NO$ requires $^m/z$ 223.09971; found: 223.09920. $\lambda_{max}$ (Cyclohexane) nm ($\epsilon$): 220.5 (14300), 239 (24000), 266.5 (3300), 276 (3700), 288 (2400), 334 (1500). Found: C, 80.55; H, 5.88; N, 6.24%. $C_{15}H_{13}NO$ requires: C, 80.69; H, 5.8; N, 6.2%. (Figures corrected for ash content (0.6%).

### Ag(I)-Promoted methanolysis of 9-chloro-1,2,3,4-tetrahydronaphthalen-1,4-imine (3b)[14]

A solution of **(3b)**[4b] (987 mg, 5.5 mmol) in dry methanol (20 ml) was added to powdered $AgClO_4$ (2.3 g, 11.0 mmol) and the mixture was stirred for 2 h at 40°C under dry nitrogen in the dark. The mixture was filtered through Celite, diluted to 100 ml with water, basified to pH 10 with 2M aqueous $K_2CO_3$, and re-filtered. The filtrate was extracted with dichloromethane (3 x 50 ml) and the combined extracts were combined, dried, and evaporated under vacuum to give the crude product (980 mg). Column chromatography (alumina, petrol → diethyl ether → methanol) gave two unidentified minor products (175 & 72 mg) and crude **(3a)** (650 mg) which was sublimed (75°C, 760 mm Hg) to give a pure sample of **(3a)**[4a] (550 mg, 70%).

### Ag(I)-Promoted methanolysis of 9-chloro-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalen-1,4-imine (4b)

The N-chloroamine **(4b)**[4b] (114 mg, 0.47 mmol) was dissolved in dry methanol (10 ml) and the solution warmed in an oil bath at 55°C. $AgClO_4$ (200 mg) was added and AgCl began to precipitate within 30 sec. The mixture was stirred for 45 min. in the dark under dry nitrogen. The dark brown mixture was filtered and evaporated to dryness. The oil was taken up in dichloromethane (20 ml) and 0.1M $K_2CO_3$ solution (20 ml) was added. The aqueous layer was extracted with further dichloromethane (3 x 20 ml). The combined organic extracts were dried and the solvent removed under reduced pressure to give a brown oil (106 mg). Preparative thick-layer chromatography (silica, diethyl ether) gave 2-methoxy-6,7-(1,4-dimethoxybenzo)-1-azabicyclo[3.2.0.]heptane **(14)** (26 mg, 23%), m.p. 67 - 68.5°C, which showed identical NMR spectra to a sample of **(14)** obtained by hydrogenation of **(9)**. The dechlorinated amine **(4a)**[4a] was also isolated (30 mg; 26%).

### Ag(I)-Promoted methanolysis of 9-chloro-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalen-1,4- imine (4b) at 0°C

The N-chloroamine **(4b)** was prepared at low temperature and the ratio of invertomers shown to be 20% *syn-* : 80% *anti-* by $^1H$ NMR spectroscopy. The sample (112 mg; 0.46 mmol) was dissolved in ice-cold dry methanol (5 ml) and added to a solution of $AgClO_4$ (110 mg) in methanol (3 ml) which was maintained at a temperature between 0°C and -10°C by means of an ice/salt bath. The heterogeneous mixture was stirred rapidly in the dark under nitrogen. The progress of the reaction was monitored by TLC and further portions of $AgClO_4$ (4 x 100 mg) were added over the next 9h. The solvent was then removed under vacuum and the residue treated with water (10 ml) and 0.1M $K_2CO_3$ solution (25 ml). The aqueous layer was extracted with dichloromethane (3 x 10 ml) and the organic extracts dried and concentrated under vacuum. The aqueous phase was basified further using 2M aq. NaOH and was extracted again with dichloromethane. The total organic extract (90 mg) was separated into its components by preparative thick-layer chromatography on silica. 2-Methoxy-6,7-(1,4-dimethoxybenzo)-1-azabicyclo[3.2.0.]heptane **(14)** (58 mg; 53%) was isolated, m.p. 67.5 - 68.5°C, undepressed on admixture with a sample of authentic **(14)**. Unchanged N-chloroamine **(4b)** was also isolated (22 mg; 20%) and was identified by $^1H$ NMR spectroscopy and mass spectrometry [$^m/z$ 239, 241 (3:1 $M^+$)].

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4. **a.** N-Alkyl derivatives: see Davies, J.W.; Durrant, M.L.; Walker, M.P.; Belkacemi, D.; Malpass, J.R. *Tetrahedron*, **1992**, *48*, 861, and references cited therein. See also footnote 4e.

**b.** N-Chloro derivatives: see Davies, J.W.; Durrant, M.L.; Walker, M.P.; Malpass, J.R. *Tetrahedron*, **1992**, *48,* 4379 and references to the work of others cited therein.

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**e.** A recent paper has included discussion of the high inversion barriers at nitrogen in N-alkyl derivatives of this ring system: Bushweller, C.H.; Brown, J.H.; DiMeglio, C.M.; Gribble, G.W.; Eaton, J.T.; LeHoullier, C.S.; Olson, E.R. *J.Org.Chem.*, **1995**, *60*, 268. The authors favour ring strain as the major cause of slow inversion, whilst acknowledging that ground state stabilisation resulting from σ-framework mixing may play a role. We retain our conviction[4c] that a major cause of the barrier-raising 'bicyclic effect'[1] lies in the unusual ground state stabilisation of these compounds and that the transition state effects (including the substantial effects of electronegative substituents) are superimposed on to this. The observed dramatic *deshielding* of the bridging nitrogen in these compounds[4c] is consistent with delocalisation of the nitrogen lone pair into the bicyclic framework, in stark contrast to the well-established *shielding* of the nitrogen in the aziridine ring system (in which high inversion barriers are indeed attributed to strain at the transition state). The CNC bond angle in the title ring system[4d] is closer to that in azetidines which do not show unusually high inversion barriers or unusual $^{15}N$ chemical shifts.

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