Solvolysis of *syn*- and *anti*-*N*-Chloro-1,4-dihydro-1,4-iminonaphthalenes

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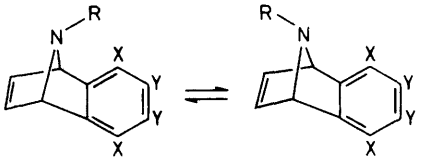
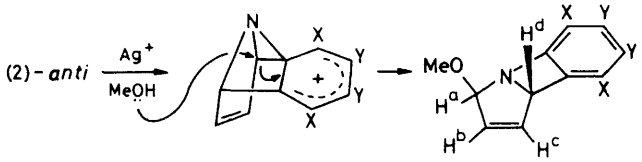
Summary The configuration of chlorine determines the course of methanolysis of the title compounds; new structures are assigned to the reaction products and the rates of reaction of the *anti*-*N*-chloroamines are shown to vary according to the ability of the substituents in the benzo-ring to encourage benzo-participation.

THE configuration of a leaving group at carbon often controls both reaction rate and product. In contrast, the preferred configuration of a leaving group at nitrogen is generally ignored since inversion at nitrogen is usually more rapid than loss of the group in question.

The high inversion barriers in the 7-azabicyclo[2.2.1]-heptane and -heptadiene systems have earlier formed the basis for studies of stereoelectronic control in reactions at nitrogen. The chlorination of (**1**) gives ratios of the *syn*- and *anti*-chloroamines (**2**) which differ under conditions of kinetic control (−50 °C; no inversion), of thermodynamic control (ambient temperature; rapid inversion), and as the electronic character of the benzo-ring is altered by substitution.[1] We have now looked at the heterolysis of the N–Cl bonds in the series of amines (**2**) under conditions of slow and rapid inversion and are able to assess the importance of π-electron participation in the loss of chloride ion and to propose firm structures for the reaction products in place of the tentative suggestions made in earlier work.[2]

Below 0 °C, the diastereoisomeric chloroamines (**2**) did not interconvert and followed different reaction pathways when





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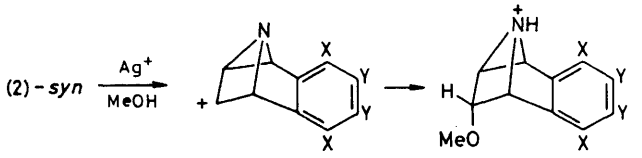
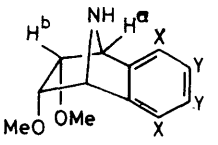


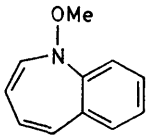


(4)

SCHEME. **a**; X = Y = H
b; X = OMe, Y = H
c; X = Y = F

treated with silver salts in methanol (Scheme). The products of participation by the aryl group in *anti*-(**2a**) and -(**2b**) were the amines (**3a**) and (**3b**); *e.g.* (**3a**), m.p. 61—62·5 °C, δ 3·38 (s, OMe), 5·00 (dt, $J_{a,d}$ 3·7, $J_{a,b}$ 1·7, $J_{a,c}$ 1·7 Hz, H^a), 5·40 (dt, $J_{a,d}$ 3·7, $J_{c,d}$ 1·7, $J_{b,d}$ 1·7 Hz, H^d), 5·52 and 5·81 (each dt, $J_{b,c}$ 5·7 with further couplings of 1·7 and 1·7 Hz, H^b and H^c), and 6·63—7·02 (ArH).† Signals due to H^a and H^d showed the greatest downfield shift on protonation with CF_3CO_2H, consistent with their close proximity to nitrogen. Spin-decoupling studies confirmed the analysis and irradiation of the benzenoid signal at δ 7·02 sharpened the signals assigned to H^d, confirming its benzylic position.

Catalytic hydrogenation of (**3a**) and (**3b**) led to the uptake of only one molar equivalent of hydrogen and yielded (**8a**) and (**8b**) which showed u.v. spectra which were identical to those of (**3a**) and (**3b**) respectively, eliminating the proposed[2] benzazepine structure (**5**) from further consideration. The n.m.r. signals due to H^b and H^c disappeared upon hydrogenation together with the homoallylic coupling[3] between H^a and H^d; (**8b**) included signals at δ 1·93—2·18 (4H, R^1—R^4), 3·48, 3·77, and 3·80 (each 3H, s, OMe), 4·64 [d, J(a, R^4) 4·6, J(a, R^2) 0 Hz, H^a], and 5·28 [d, J(d, R^1) 7·6, J(d, R^3) 0 Hz, H^d]. The observed zero vicinal coupling constants define the corresponding bond angles and hence the conformation of the pyrrolidine ring. The analysis was confirmed by catalytic addition of deuterium which yielded a mixture of (**9b**) and (**10b**) in a 55 : 45 ratio showing δ 4·63 [H^a: d, J(a, R^4) 5 Hz for (**9b**) and s for (**10b**)] and 5·27 [H^d: s for (**9b**) and d, J(a, R^1) 8·3 Hz for (**10b**)]. The stereochemistry of the methoxy-group follows unambiguously from these data and is mechanistically reasonable. The same analysis applies to (**3a**) which gave a 24 : 76 mixture of (**9a**) and (**10a**).



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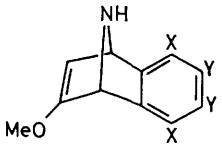

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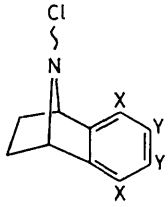

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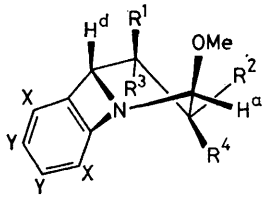

(8) $R^1 = R^2 = R^3 = R^4 = H$
(9) $R^1 = R^2 = D$, $R^3 = R^4 = H$
(10) $R^1 = R^2 = H$, $R^3 = R^4 = D$

a; X = Y = H
b; X = OMe, Y = H
c; X = Y = F

† The n.m.r. spectrum of (**3a**) in $CDCl_3$ was as described in reference 2. However, measurement at 400 MHz in C_6D_6 solvent allowed the first-order analysis quoted above. The spectrum of (**3b**) was similar but signals assigned to H^c and H^d overlapped.

The *syn*-invertomers of (**2a**—**c**) reacted with silver salts in methanol below 0 °C to yield, after basification, the amines (**4a**—**c**); *e.g.* (**4b**) *m/e* 265 (M^+), 234, 218, and 177; ν_{max} (CH_2Cl_2) 3290 cm^{-1}: δ 6·62 (s, 2H, ArH), 4·78 (m, 2H, H^a), 4·08 (m, 2H, H^b), 3·75 (s, 6H, ArOMe), 3·42 (s, 6H, OMe), and 2·06 (br, s, NH, exchangeable with D_2O). These compounds are presumably formed by participation of the π-electrons of the etheno-bridge in loss of Cl^- (Scheme).‡

When Ag^+-promoted reactions were followed by n.m.r. spectroscopy in CD_3OD at low temperatures, (**2b**) was found to be considerably more reactive than (**2a**); indeed, in this case, *anti*-(**2b**) disappeared more rapidly than the *syn*-isomer, showing the profound effect of a methoxy-group in encouraging benzo-participation. In contrast, *anti*-(**2c**) was unreactive at low temperatures and no (**3c**) was observed under any conditions; (**4c**) and (**1c**) were the sole products.

The higher reactivity of the *syn*-invertomers of (**2a**)[2] and (**2c**) was confirmed by solvolysis experiments in methanol at ambient temperature (without silver salt) which led to the formation of (**4a**) and (**4c**),‡ with no observable (**3**). Clearly the *anti*-invertomer reacts *via* prior inversion to *syn*, given the opportunity. However, in the case of (**2b**), the benzo-participation route was competitive even under conditions of rapid inversion, giving both (**3b**) and (**4b**). Indeed, the higher reactivity of the dimethoxybenzo-group was sufficient to promote the reaction of a sample of (**7b**) under conditions of rapid inversion giving (**8b**) directly. Neither (**7a**) nor (**7c**) was reactive under these conditions.

We thank Drs. O. Howarth and E. Curzon for the 400 MHz n.m.r. spectra. We are grateful to the S.E.R.C. for access to the high-field n.m.r. facilities at the University of Warwick and for a Research Studentship (to M.L.D.).

(*Received*, 22*nd July* 1981; *Com.* 876.)

‡ Quantities of (**1**) were formed in these reactions. N.m.r. spectra of mixtures of (**4a**) and (**1a**) showed a pattern of signals which was similar in some, but not all, respects to that described for (**6**)[2] but we have been unable to detect (**6**) in any of these reactions.

[1] J. R. Malpass and M. P. Walker, *J. Chem. Soc., Chem. Commun.*, 1979, 585.
[2] V. Rautenstrauch, *Chem. Commun.*, 1969, 1122. Some unease concerning structure (**5**) was expressed when our solvolysis work was in its early stages (V. Rautenstrauch, personal communication).
[3] Compare with *trans*-homoallylic coupling in 1,2-fused-2,5-dihydropyrroles such as retronicine (3·5 Hz): C. C. J. Culvenor, M. L. Heffernan, and W. G. Woods, *Austr. J. Chem.*, 1965, **18**, 1605, 1625.