

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

By MICHAEL L. DURRANT and JOHN R. MALPASS*

(*Department of Chemistry, Leicester University, Leicester LE1 7RH*)

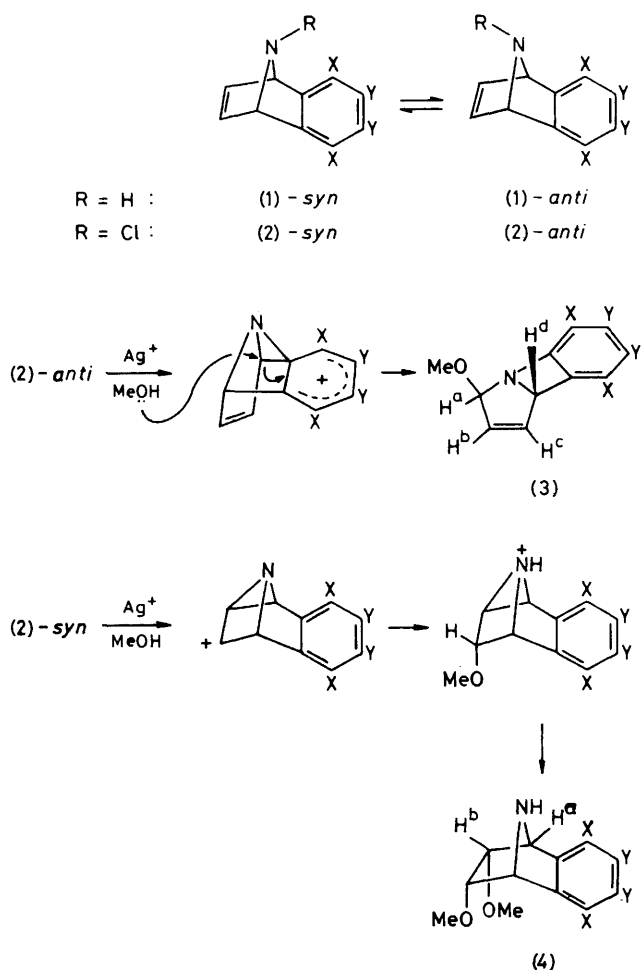
Summary The configuration of chlorine determines the course of methanolysis of the title compounds; new structures are assigned to the reaction products and the

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

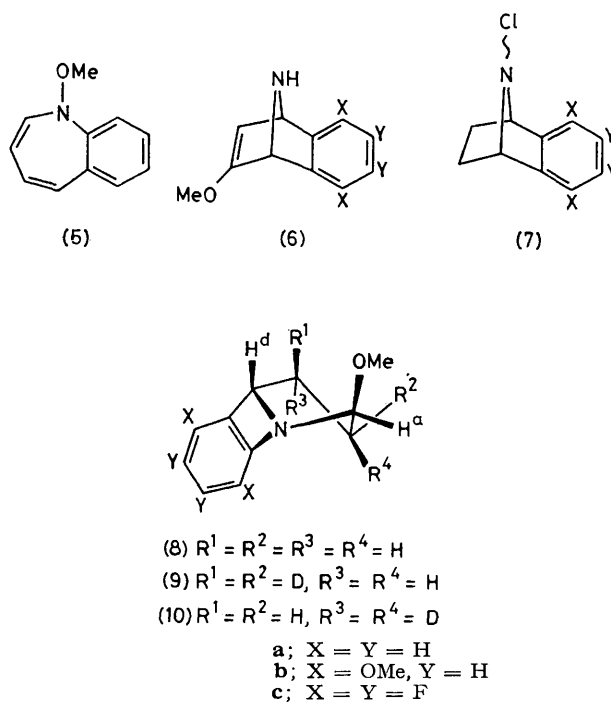
Below 0°C , the diastereoisomeric chloroamines (2) did not interconvert and followed different reaction pathways when



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. $61-62.5^{\circ}\text{C}$, 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 $\text{CF}_3\text{CO}_2\text{H}$, 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 proposed² 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 coupling³ between H^a and H^d; (8b) included signals at δ 1.93–2.18 (4H, R¹–R⁴), 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).



† 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} (CH₂Cl₂) 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 D₂O). 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 CD₃OD 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.

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[‡] 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.