Intramolecular π-Participation in Displacement of a Nucleofuge from Nitrogen

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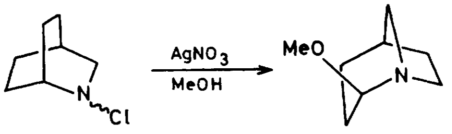
Intramolecular participation of π-electrons controls the Ag^I-assisted heterolysis of unsaturated cyclic *N*-chloroamines; molecular rearrangement of a rigid *N*-chloroamine occurs in the absence of Ag^I with involvement of a suitably-oriented π-bond.

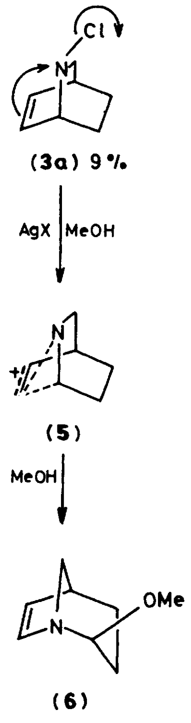
Skeletal rearrangements occur during the reactions of a number of *N*-chloroamines with silver salts *e.g.* (**1**) → (**2**).[1] The idea of discrete nitrenium ions as reaction intermediates remains controversial and a significant amount of σ-participation in the removal of chloride ion by Ag^I is even more attractive here than in corresponding carbon analogues in view of the lesser ability of nitrogen to stabilise a positive charge. Intramolecular π-participation in Ag^I-catalysed heterolysis of N–Cl bonds has seen little study, in contrast to the intramolecular involvement of π-bonds in homolytic reactions of *N*-chloroamines which is well documented.[2] We have shown that participation by alkene and arene π-electrons plays a key role in the rearrangements of *N*-chloro-1,4-dihydro-1,4-iminonaphthalenes.[3] We now show that this is a more general phenomenon and report examples which demonstrate (i) the relative importance of σ- and π-participation in the heterolysis of N–Cl bonds, (ii) a comparison of π-participation in displacement of chloride ion from nitrogen *vs.* displacement from carbon, and (iii) that a suitably-oriented π-bond can induce molecular rearrangement in the absence of Ag^I salts and with only moderate thermal activation.

Whilst the cyclic *N*-chloroamine (**3**) exists predominantly as the *endo*-invertomer (**3b**),[4] this is in rapid equilibrium with the *exo*-invertomer (**3a**) at ambient temperatures. Competition between two possible reaction pathways can thus readily be assessed by product studies (in contrast with carbocyclic analogues for which kinetic comparisons are necessary).



(**1**) (**2**)

Participation of the σ-bond as shown in Scheme 1 would parallel the observed behaviour of (**1**) and would be expected to lead even more readily to the formation of methyl ethers *via* the allylic carbenium ion (**4**); π-participation, on the other hand, would lead to (**6**) *via* the intermediate represented as (**5**). In fact, treatment of (**3**) with $AgClO_4$–MeOH gave only (**6**) in 94% yield (56% after preparative g.l.c.). Thus the chloride ion is removed specifically from the minor invertomer (**3a**). This degree of discrimination argues against simple heterolysis of the N–Cl bond to give a discrete nitrenium ion and in favour of a substantial degree of π-participation and hence delocalization of the developing positive charge. The rearrangement of (**7**) in $AgNO_3$–MeOH occurs readily within 90 min at 40 °C (but with some decomposition) to give (**8a**) 42%, (**8b**) 1.5, and (**10a**) 14, which could be separated only by preparative g.l.c. Longer reaction times led to lower yields of (**8a**) suggesting that (**8a**) was a possible precursor of (**10a**). The matter was clarified as a result of the discovery that (**7**) can be

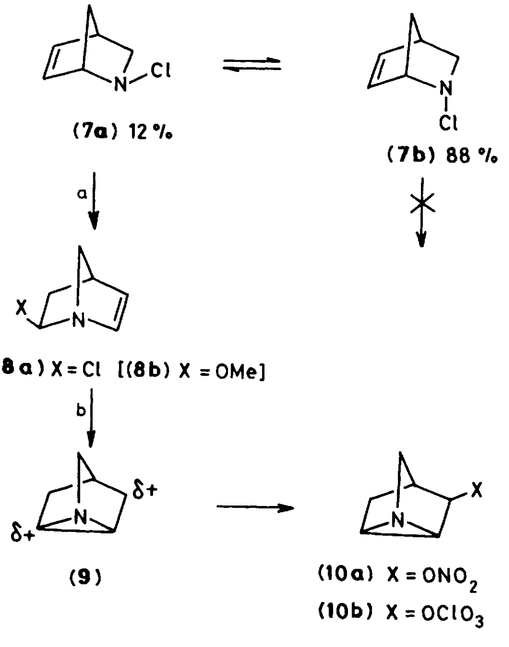


Scheme 1

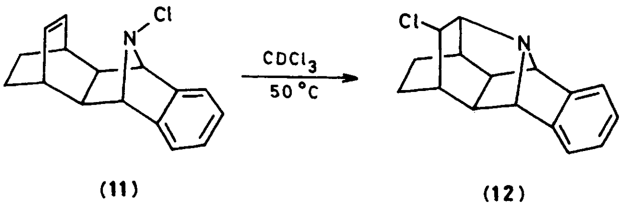
converted cleanly into (**8a**) on alumina.[5] The pure *C*-chloro-compound (**8a**) was then converted, in turn, into (**10a**) on warming in dry MeOH with an excess of powdered $AgNO_3$ (33% isolated crude yield).†

Whilst some direct conversion of (**7a**) into (**10a**) cannot be ruled out, the isolation of (**10a**) provides direct evidence for the involvement of the ion (**9**) which has recently been proposed (but not directly detected) as an intermediate in the complex solvolysis of the *N*-tosylamine corresponding to (**7**).[6] Scheme 2 could be rationalised as involving (**9**) as an intermediate in both steps a and b under $AgNO_3$ catalysis giving (**8a**) from an intimate ion pair under kinetic control and yielding (**10a**) under thermodynamic control, although the degree of charge build-up at the transition state of step a must be limited since much of the chlorine is retained in the product rather than being lost as AgCl. The isolation of (**8a**) makes it clear that, in the silver-ion-catalysed reaction, the rate constant for step a (N–Cl cleavage with π-assistance) is greater than that for step b (C–Cl cleavage with π-assistance).

These demonstrations that suitably-oriented π-electrons can control the displacement of a nucleofuge from nitrogen led us to examine the compound (**11**) in which the alkene is well placed to interact with the nitrogen. Thus (**11**) was prepared by cycloaddition of cyclohexa-1,3-diene with 1,4-dihydro-1,4-iminonaphthalene followed by chlorination of the secondary amine with *N*-chlorosuccinimide. On warming to 50 °C in $CDCl_3$, the clean conversion of (**11**) into (**12**) could be



Scheme 2. *Reagents:* step a: either neutral alumina or $AgNO_3$–MeOH; step b: $AgNO_3$–MeOH.



monitored by n.m.r. spectroscopy; the reaction was complete within 7 h to give (**12**) as the sole isolated product.‡

There are clear parallels between these reactions (in which a group is displaced from nitrogen, reversing the usual nucleophilic character of this atom) and the extensively-studied solvolytic reactions of bicycloheptenyl and bicyclo-octenyl systems; the conversion of (**11**) into (**12**) also finds a close analogy in carbocyclic systems.[7] In practical terms, migration of sp^3 carbon to electron-deficient nitrogen has seen some attractive synthetic development[8] and, in a similar fashion, participation of neighbouring π-electrons in displacements from nitrogen merits further attention as a means of forming intramolecular C–N bonds.

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† Work with $AgClO_4$ was suspended when a crystalline sample of (**10b**) exploded without warning in the freezer compartment of a refrigerator.

‡ Compound (**11**) reacts here under conditions which leave intact similar amines lacking a proximate π-bond; unassisted heterolysis or homolysis therefore appear unlikely.

Added in proof: Very recent work (R. E. Moss and J. R. Malpass) has shown that the efficient conversion of (**11**) into (**12**) can be induced by Ag^I salts and also, suprisingly, by acid (*e.g.* 1 mol equiv. trifluoroacetic acid in $CDCl_3$ at ambient temperature) in the absence of radical initiators. Homolytic and/or electrophilic chlorination mechanisms deserve consideration under acidic conditions (see ref. 2 for a summary of existing work in this area). Investigations are under way on the mechanistic consequences of variations in reaction conditions and on the extent to which the enforced interaction between the π-bond and the nitrogen lone pair may be responsible for the unusual behaviour of (**11**).

We thank the S.E.R.C. for studentships to M. L. D. and M. P. W. and the S.E.R.C. high-field n.m.r. service at Warwick for 400 MHz spectra of (**12**). Detailed analysis of n.m.r. spectra of the compounds described in this work will be decribed in the full paper.

Received, 18th February 1985; Com. 212

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