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CHLOROAZIRINES - CONVERSION TO AZACYCLOPROPENIUM CATIONS AZIDOAZIRINES AND BIAZIRINES

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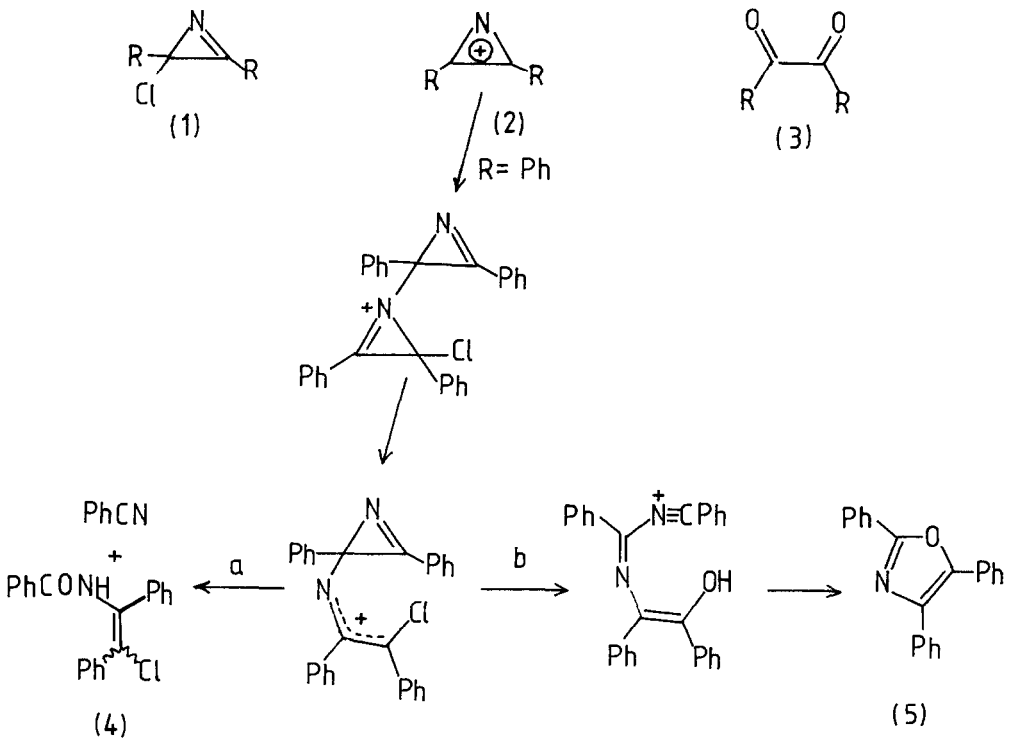
Summary : Chloroazirines ionise readily but the derived azacyclopropenium ions cannot be observed directly; attempted conversion to biazirines gives the pyrazine and pyrimidine and reaction with azide ion leads to alkynes and nitriles via labile azidoazirines.

Chloroazirines[1] are obvious precursors to azacyclopropenyl cations. Although calculations predict considerable resonance stabilisation[2] such cations have received little attention; they have however been suggested as intermediates in a number of reactions.[3]

Two problems might arise in the generation of stable azacyclopropenyl cations (2) from chloroazirines (1) which do not apply in the case of cyclopropenyl cation formation from cyclopropenyl halides. Firstly the N-lone pair on the azirine (or even the azacyclopropenyl cation) is likely to lead to polymerisation by attack on the electrophilic cation. Secondly Lewis acid catalysts added to promote ionisation of the chloride can also lead to polymerisation by preferential coordination to the azirine N.

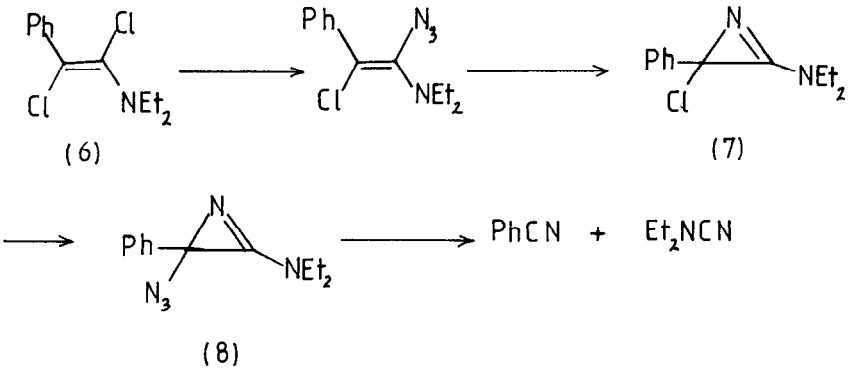
Chlorodimethylazirine (1; R=Me) is unionised in SO_2ClF at -60^0C; two singlets at 3.00 and 2.35 δ being observed in the $^1H.m.r.$ spectrum. In liquid SO_2 these signals rapidly disappear giving a very complex spectrum and no indication of the symmetrical cation. Chlorodiphenylazirine (1; R=Ph) behaves similarly, removal of SO_2 and quenching with water gives PhCN (50%) and the N-vinyl amide (4)[4] (52%) which can be accounted for as shown in the Scheme path a. Addition of either $SbCl_5$ or $AlCl_3$ to the chloroazirines (1; R=Me;Ph) gives only polymeric material. Treatment of (1; R=Ph) with an equivalent of $AgBF_4$ in MeCN gives silver chloride (30%), and benzil (3; R=Ph), triphenyl oxazole (5) and benzonitrile in proportions which are highly dependent on the concentration of reactants and rate of mixing. Although benzil could have arisen from the cation (2; R=Ph), the presence of benzonitrile and oxazole again indicates that attack of chloroazirine on cation is a major probelm (Scheme path b). Slow addition of (1; R=Ph) to a three fold excess of $AgBF_4$ in MeCN (to ensure that any cation produced was exposed to the minimum of chloroazirine) caused rapid precipitation of AgCl (75%). Formation of the cation (2; R=Ph) is supported by quenching of the colourless filtrate with H_2O which causes an immediate colour change to yellow and formation of benzil, again in high yield (75%). Unfortunately the solution was necessarily too dilute for satisfactory n.m.r. study and attempted concentration of the presumed cation solution led only to hydrolysis.

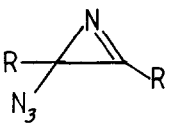


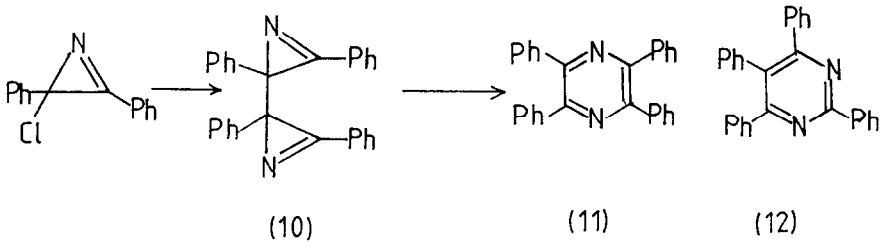
The alternative approach to cation (2; R=Ph) involving hydride abstraction from 2,3-diphenylazirine with trityl tetrafluoroborate also failed. Thus in MeCN 2-methyl-4,5-diphenylimidazole was formed by the trityl cation acting as Lewis acid catalyst for addition of the solvent to the azirine. In SO_2 some triphenylmethane (16%) was observed together with tetraphenylpyrazine (14%) indicating again that if cation (2) is formed it is intercepted by unchanged azirine.

An amino substituent considerably stabilises the cyclopropenyl cation system.[5] An attempt was therefore made to produce the chloroaminoazirine (7) by treatment of the α-chloroenamine (6)[6] with azide ion. Cyclisation of α-azidoenamines to azirines is spontaneous at low temperature[7] and presumably occurs in this case. However, the only product isolated, even with a deficiency of azide ion, is the azidoazirine (8)[8] together with unreacted (6). Clearly the anticipated stabilisation of the azacation by the diethylamino group has been achieved, this being reflected in the greater lability of the chlorine in (7) than in (6).

The azido azirine (8) is itself of interest since by analogy with cyclopropenyl azides which thermally rearrange to 1,2,3-triazines[9] it is a potential precursor to a 1,2,3,4[10] or 1,2,3,5-tetrazine.[11] However in refluxing CCl_4 (8) is rapidly converted into diethyl cyanamide (87%) and benzonitrile (96%)







Similar fragmentation occurs at even lower temperature with the azidoazirines (9, R=Ph[12] and p-MeC_6H_4[13]) produced from the chloroazirines (1) and azide ion. In all cases a careful search for the acetylene which would have revealed expansion to an unstable 1,2,3,4-tetrazine prior to fragmentation showed none to be formed. Although we cannot rule out fragmentation via a 1,2,3,5-tetrazine we favour a mechanism involving loss of nitrogen in concert with cheletopic extrusion of the nitrile from the azirine.[14]

The chloroazirines (1) are attractive precursors to biazirines[15], eg (10), nitrogen analogues of bicyclopropenes whose rearrangement to benzenes has received considerable attention.[16] Chloroazirine was consumed within 30 min at room temperature on treatment with an excess of lithium in THF. No biazirine (10) was detected; however, tetraphenylpyrazine (11) (10%) and tetraphenylpyrimidine (12)

(10%), possibly formed by aromatisation of the biazirine (10) were isolated. No tetraphenylpyridazine was formed.

References and Notes

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12. Pale yellow oil, νmax 2190(N_3), 1725 (C=N)cm^{-1}.
13. Pale yellow oil - too unstable for determination of spectral data.
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