An Aza-analogue of the Cyclopropyl to Allyl Cation Rearrangement

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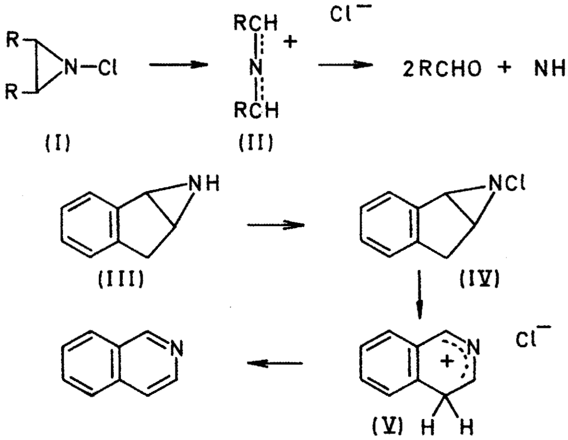
Summary The N-chloro-derivative of indano [1,2-*b*]aziridine undergoes spontaneous dehydrochlorination to give isoquinoline, in an aza-analogue of the cyclopropyl to allyl cation rearrangement.

GASSMAN and Dygos[1] have recently suggested that the solvolysis of N-chloroaziridines (I) is an electrocyclic process, with the same orbital symmetry control as the cyclopropyl to allyl cation rearrangement.[2] However, their suggested intermediate (II) was extensively decomposed, as shown, under the solvolysis conditions. It seemed that this mechanism might be supported by the choice of a structure for intermediate (II) which could be readily stabilised, for example by proton loss, before hydrolysis occurs. Such support is provided as follows.

Indene was converted in 90% yield into indano[1,2-*b*]-aziridine (III) by addition of iodine azide followed by reduction with LiAlH_4.[3] Aziridine (III) is a colourless oil, picrate m.p. 240—245°, which is fairly stable in ice-cold solution under nitrogen. Treatment of (III) with sodium hypochlorite in aqueous ethanol at 0° or with t-butyl hypochlorite in methylene chloride at $-60°$ gave the N-chloro-derivative (IV) as a colourless unstable oil [no N–H absorption; m/e 167, 165; 130 ($P^+ - \text{Cl}$) (base peak); 129 ($P^+ - \text{Cl} - \text{H}$)]. On being warmed to room temperature in aqueous methanol, (IV) lost hydrogen chloride to give isoquinoline, in 10—15% yield after purification. This rearrangement is isoelectronic with the well-known conversion of the indene-dichlorocarbene adduct into 2-chloronaphthalene.[4] Presumably the mechanism is very similar, involving the nitrenium ion (V) which is the equivalent of (II) above.†



Although many cyclopropyl to allyl rearrangements of fused halogeno-cyclopropanes have been reported,[5] this appears to be the first comparable expansion of a heterocyclic ring.

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† The slow step in the conversion of (IV) into isoquinoline may well be inversion of the *exo*- to the *endo*-chloride (*cf.* S. J. Brois, *J. Amer. Chem. Soc.*, 1968, **90**, 506, 508, 1680) required for the necessary disrotatory opening of (IV) to (V).

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