A Novel Ring-opening Reaction of an Aziridinium–$AlCl_3$ Complex. Reaction of Phenyl Azide with Alkenes in the Presence of $AlCl_3$

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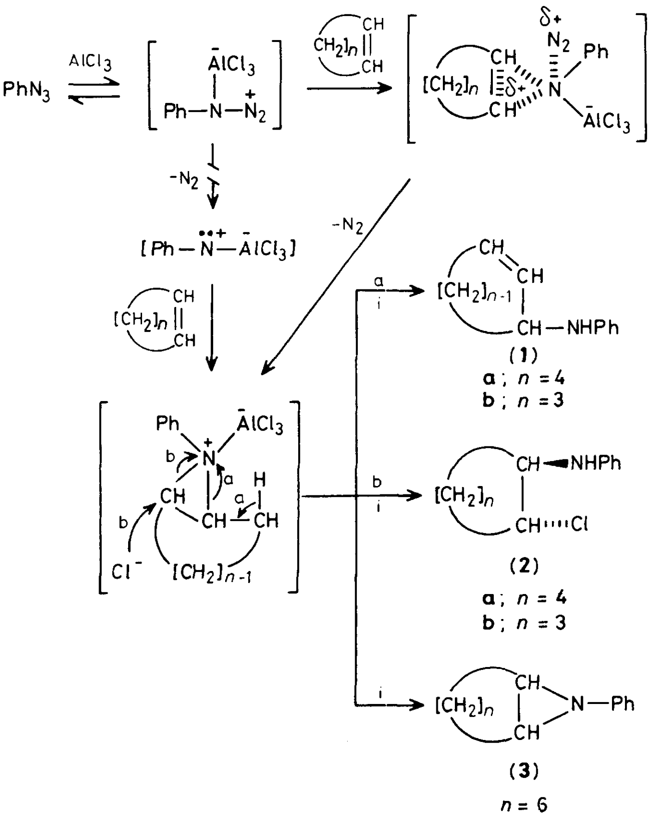
Reaction of phenyl azide with alkenes in the presence of $AlCl_3$ gives an aziridinium–$AlCl_3$ complex *via* an azide–$AlCl_3$ complex; this reaction is followed by ring-opening reactions of the aziridinium–$AlCl_3$ complex to give *N*-allylanilines and/or *N*-phenyl-β-chloroamines after work-up with aqueous Na_2CO_3, but the reaction with *cis*-cyclo-octene yields a novel aziridine, 9-phenyl-9-azabicyclo[6.1.0]nonane after the work-up.

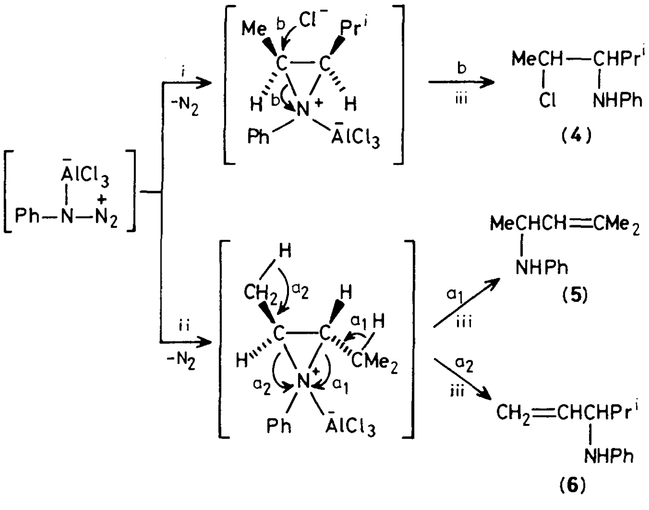
Aromatic Friedel–Crafts *N*-substitution by either hydrazoic acid[1] or organic azides[2—7] has literature precedent. We have recently reported that aromatic *N*-substitution occurs *via* arylnitrenium–$AlCl_3$ complexes generated from aryl azides in the presence of $AlCl_3$.[8] The work has been extended to the novel formation of an aziridine in the presence of alkene, and subsequent ring-opening reactions.

To a stirred suspension of $AlCl_3$ (2.6 mmol) in cyclohexene (0.7 ml)–CH_2Cl_2 (2.0 ml) a solution of phenyl azide (2.3 mmol) in cyclohexene (1.1 ml)–CH_2Cl_2 (1.0 ml) was added over a period of *ca.* 5 min. The reaction temperature rose from 15 to *ca.* 30 °C owing to the heat of reaction, and then the evolution of N_2 gas ceased. After addition of aqueous Na_2CO_3 solution, 3-(phenylamino)cyclohexene (**1a**) (49%) and *trans*-1-chloro-2-(phenylamino)cyclohexane (**2a**) (43%) were separated by preparative g.l.c. from the resulting organic layer. Similarly, the reaction with cyclopentene or *cis*-cyclo-octene gave 3-(phenylamino)cyclopentene (**1b**) (26%) and *trans*-1-chloro-2-(phenylamino)cyclopentane (**2b**) (26%) or a new aziridine, 9-phenyl-9-azabicyclo[6.1.0]nonane (**3**) (47%), respectively (Scheme 1). A similar reaction with *cis*-4-methylpent-2-ene yielded 2-chloro-4-methyl-3-(phenylamino)pentane (**4**) (31%), but only traces of 2-methyl-4-(phenylamino)pent-2-ene (**5**) and 4-methyl-3-(phenylamino)pent-1-ene (**6**) were observed. However, with the *trans*-alkene, compounds (**5**) and (**6**) were formed in 23 and 20% yields respectively (Scheme 2). The structures of the products were confirmed by i.r. and ^1H and ^{13}C n.m.r. spectroscopy.

The formation of aziridine (**3**) without contamination by ring-opening products in the reaction with *cis*-cyclo-octene suggests that the reaction proceeds *via* aziridinium–$AlCl_3$ complex formation. The ring strain in the three-membered ring is greater for the 5,3 and 6,3 fused rings than for the 8,3 fused ring, because of the proximity of the adjacent hydrogens close to the aziridine ring: molecular models of the aziridinium–$AlCl_3$ complexes show the nitrogen atom adjacent to the hydrogens, and the distance between the nitrogen and the hydrogens is long in the *cis*-cyclo-octene complex compared to the cyclohexene and cyclopentene complexes. Thus, the cyclopentene and cyclohexene complexes may undergo concerted ring-opening to give (**1a**)† or (**1b**)† (see path a, Scheme 1), and an S_N2 ring-opening *via* the chloride anion‡ to yield the



Scheme 1. *Reagent:* i, aqueous Na_2CO_3.



Scheme 2. *Reagents:* i, *cis*-4-methylpent-2-ene; ii, *trans*-4-methylpent-2-ene; iii, aqueous Na_2CO_3. Only traces of (**5**) and (**6**) were formed from i.

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† These products were not formed from the corresponding *N*-phenyl-β-chloroamines under these reaction conditions without the azide and the alkenes. No formation (see ref. 9) of alkylidenephenylamines was observed which could conceivably be formed *via* secondary carbocations, the *trans*-addition giving (**2**), and the regiospecific reaction producing (**4**) presumably eliminating an S_N1 ring-opening mechanism.

‡ The anion eliminated from the complex appears to be Cl^-.

trans-adduct§ (**2a**) or (**2b**) (path b, Scheme 1). The *cis*-cyclooctene complex would be inert to the ring-opening reaction.

Additions to *cis*- and *trans*-4-methylpent-2-enes are completely stereospecific, leading to aziridinium–$AlCl_3$ complexes in which the alkyl groups have the same geometry as in the alkenes. The complex formed from the *cis*-alkene¶ is attacked by a chloride anion preferentially at the less hindered carbon (*i.e.* C-3) to produce (**4**) (path b, Scheme 2). However, the complex formed from the *trans*-isomer is not susceptible to such an attack because of steric interference between the attacking anion and the 3-Me or 2-Pr^i, so that the concerted ring-opening leads to (**5**)† and (**6**)† (paths a_1 and a_2, Scheme 2).

Decomposition of the azide in the presence of cyclohexene occurs much faster than in the presence of benzene. This indicates that the decompositions occur *via* different mechanisms. An azide–$AlCl_3$ complex spontaneously loses a molecule of N_2 in the presence of benzene to form a nitrenium–$AlCl_3$ complex.[8] Therefore, such a loss of N_2 can be ruled out in the presence of alkene, and a molecule of N_2 should be eliminated by attack of an alkene on the azide–$AlCl_3$ complex|| to form the aziridinium–$AlCl_3$ complex, because the alkene is more nucleophilic than benzene.

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§ The coupling constant between 1-H and 2-H in (**2a**), $J_{1,2}$ 8 Hz, shows the protons to be axial (*i.e.* *trans*-geometry). The preferential *trans*-addition (no formation of the *cis*-adduct) as observed by g.l.c. and ^{13}C n.m.r. spectra supports the S_N2 ring-opening.

¶ A low yield of (**5**) and (**6**) from the *cis*-alkene probably arises from steric crowding in the transition state leading to the intermediate.

|| The $AlCl_3$-catalysed decomposition occurs *via* an azide–$AlCl_3$ complex.