Rearrangement of 1-Azidoadamantane to 3-Aryl-4-azahomoadamantane in the Presence of Aluminium Chloride and Aromatic Substrates

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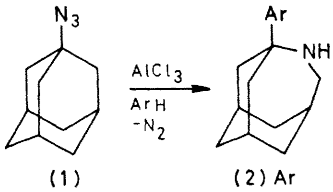
Summary Reaction of 1-azidoadamantane with aromatic substrates in the presence of aluminium chloride gave the corresponding 3-aryl-4-azahomoadamantane, presumably *via* an imine intermediate.

Alkyl azides are reported to undergo reactions involving elimination of nitrogen gas, azide ion, or both, in the presence of aluminium chloride and benzene.[1,2] The resulting products were *N*-alkylanilines, imines from rearrangement, or alkylbenzenes. The imines apparently did not participate in Friedel–Crafts alkylation. We report the first reaction of an alkyl azide with aromatic compounds catalysed by aluminium chloride, resulting in rearrangement followed by aminoalkylation of the aromatic reagent.

When 1-azidoadamantane (**1**) was exposed at 80 °C for 1·25 h to aluminium chloride in the presence of an aromatic substrate ArH (1-AdN$_3$:AlCl$_3$:ArH = 1:10:73 molar), the corresponding 3-aryl-4-azahomoadamantane (**2**) was formed in >90% yield [*ortho*:*para* (**2b**) *ca* 1:1, (**2c**), *ca* 1:1·86]. Halogen analysis (micro) of products obtained from competition reactions (PhMe/PhCl) gave relative rate data indicating that the attacking electrophile possesses rather high activity, similar to certain nitrating and halogenating species investigated by Olah and his co-workers.[3,4] All products gave acceptable elemental analysis and n.m.r., i.r., and mass spectral data.



(1)

(**1**) (**2**) Ar
a, Ph
b, C_6H_4Me
c, C_6H_4Cl

When the imine prepared from cyclohexanone and cyclohexylamine[5] was similarly treated, no substitution occurred. In fact it has been reported that cyclohexyl azide in the presence of aluminium chloride and benzene gave rearrangement products, namely, the corresponding ring-expanded imine (30–40%) and cyclohexanone imine (15%) as well as cyclohexylbenzene (30%).[2] With the exception of the Pictet–Spengler[6–8] and analogous reactions, which are intramolecular processes usually involving highly activated aromatic nuclei, the literature apparently contains no examples of intermolecular, Friedel–Crafts substitution in the benzene series by imines. (1-Pyrroline is reported to undergo condensation with pyrrole and indole in the absence of an acidic catalyst.[9] However, the reactivity of this imine is quite limited as demonstrated by its inertness toward 1-methylpyrrole or carbazole.) Since nitrogen gas, not azide ion, is generated in the reaction described in equation (1), it is reasonable, based on prior work,[2] to propose the intermediacy of an imine complexed with the Lewis acid catalyst. Acid-catalysed decomposition of azides displays second-order kinetics,[10] pointing to participation of a nitrene complexed (nitrenium ion) with the Lewis acid catalyst,[2] perhaps in a concerted process.

The literature contains other reports of rearrangement of (**1**) leading to azahomoadamantanes. For example (**1**) on photolysis[11] in the presence of methanol produced the corresponding 3-methoxy-4-azahomoadamantane; in non-hydroxylic media, the dimer of the bridgehead imine resulted With sulphuric acid, 3-hydroxy-4-azahomoadamantane is formed[12] Analogously, 1-*NN*-dichloroaminoadamantane, on rearrangement with aluminium chloride, followed by treatment with nucleophiles, such as water, alcohol, thiols, or aromatic compounds, gave the corresponding 3-substituted-4-azahomoadamantanes[13]

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