Generation and Reactivity of 4-Azatricyclo[5.3.1.$1^{3,9}$]dodec-3-ene and 5-Azatricyclo[4.4.1.$1^{3,9}$]dodec-5-ene, New Bridgehead Imines

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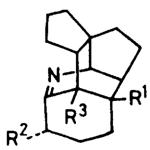
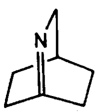
Summary The title bridgehead imines have been generated in a ratio of 1 : 2 by photolysis of 3-azidohomoadamantane; their chemical reactivity is described.

THE synthesis and chemistry of bridgehead alkenes (anti-Bredt's rule olefins) have been much studied for the past fifty years.[1] However, studies on bridgehead imines seem to have been limited to the isolation of the 2-azabicylo[3.3.1]-non-1-ene system (**1**) by Toda *et al.*[2] and the first synthesis of bicyclo[3.3.1]non-1-ene.[3] The photolysis of appropriate bridgehead azides is known to be a simple and promising route to the corresponding bridgehead imines as demonstrated by the photolysis of 1-azidonorbornane to (**2**) and (**3**),[4] 1-azidoadamantane to (**4**),[5] and 9-azidotriptycene to (**5**).[6] We now report the photolysis of the 3-azidohomoadamantane (**6**)[7] to two new bridgehead imines (**7**) and (**8**).



(1)



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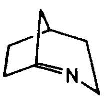

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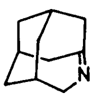

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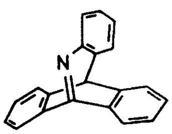

(5)

A methanol solution of (**6**) was irradiated for 3 h (100 W high pressure Hg lamp, Vycor filter) in view of the fact that highly strained imines (**2**)—(**5**) can be trapped efficiently by methanol.[4-6] After removal of the solvent, the crude product was analysed by i.r. (film) and ^{1}H n.m.r. ($CDCl_3$) spectroscopy: the i.r. spectrum showed a C=N stretching band (1650 cm^{-1}) but no azide band (2100 cm^{-1}), and the ^{1}H n.m.r. spectrum did not exhibit the sharp singlet signals at δ 3·0—3·5 of the expected OMe group of (**9**) and (**10**). These facts indicated that the imines (**7**) and (**8**) were generated from (**6**) but they did not react with methanol being less reactive than the imines (**3**)—(**5**). However, attempted purification of (**7**) and (**8**) on an alumina column was unsuccessful because of their decomposition to an intractable solid. In order to trap the imines by hydride, (**6**) was irradiated in the presence of an excess of $NaBH_4$ [10-fold molar excess with respect to (**6**)] in MeOH. Analyses of the product by g.l.c. and ^{1}H n.m.r. spectroscopy indicated the formation of 4-azatricyclo[5.3.1.$1^{3,9}$]dodecane (**11**)[8] and 5-azatricyclo[4.4.1.$1^{3,9}$]dodecane (**12**) in a ratio of 1 : 2 (70%). The amine (**12**) was isolated after preparative g.l.c. as a colourless solid, m.p. 234—237 °C, picrate m.p. 280—282 °C;† ^{1}H n.m.r. δ 3·60 (br s, 1), 3·02 (d, 2, J 4·5 Hz), 2·73 (s, 1, exch.), and 2·5—0·5 (m, 15). Evidence for the formation of both bridgehead imines (**7**) and (**8**) was thus obtained from their reduction to the corresponding amines (**11**) and (**12**). Furthermore, irradiation of (**6**) in the presence of a 20-fold molar excess of NaCN using a two-phase system (n-hexane–water), catalysed with Adogen 464, afforded the aminonitriles (**13**) and (**14**) ($\nu_{C\equiv N}$ 2140 and 2210 cm^{-1}) in *ca.* 1 : 2 ratio but their purification on a silica gel column failed because of decomposition. Sublimation of the crude product at 160 °C (0·3 mm) afforded (**14**) as a colourless solid (53%): m.p. 136—139 °C; i.r. (KBr) 3400 and 2210,

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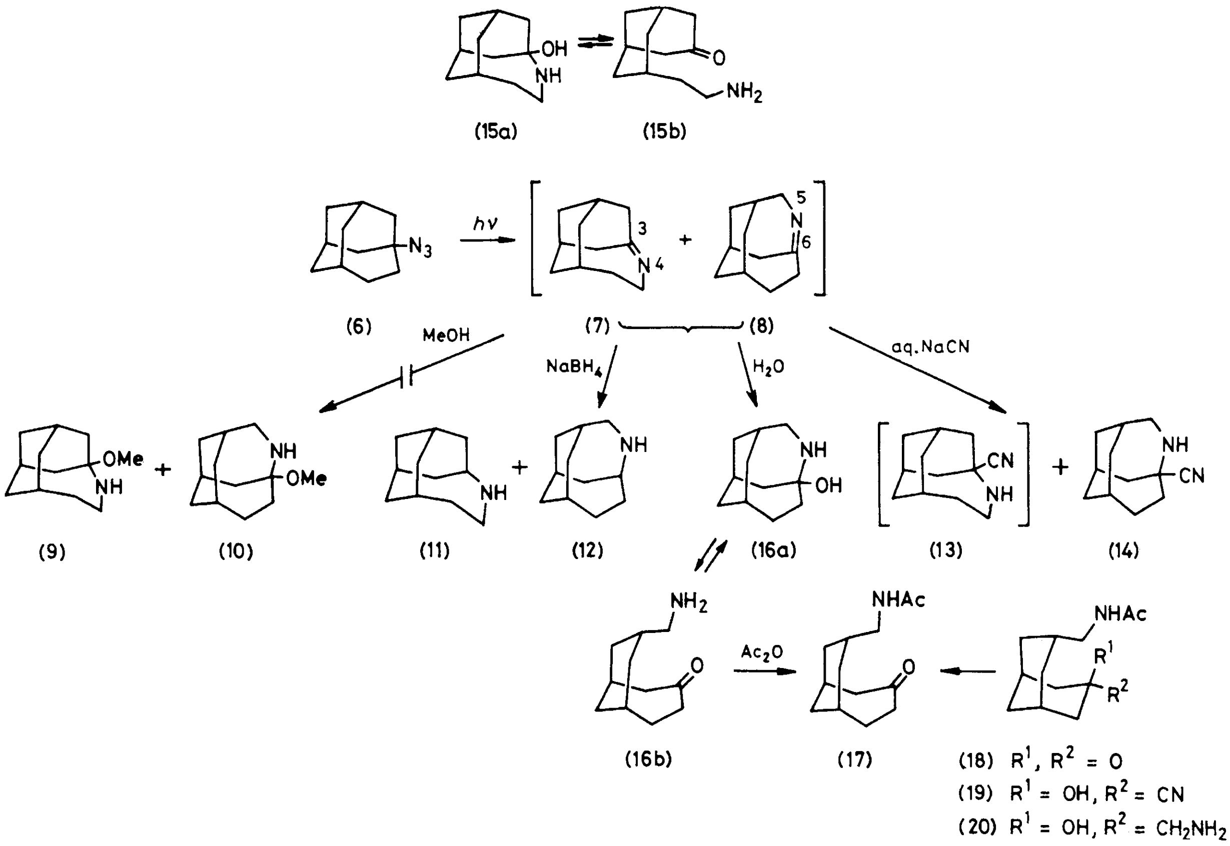
† All new compounds described here had spectral and microanalytical properties in agreement with the assigned structures.



Scheme

cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) δ 3·02 (d, 2, J 4·0 Hz), 1·55 (s, 1, exch.), and 2·5—0·9 (m, 15). The given structure (**14**) was corroborated by ^{13}C n.m.r. data (11 lines, 12 C). The non-isolation of (**13**) may be due to its decomposition during the work-up.

Hydration to (**7**) and (**8**) was also examined by photolysis of (**6**), in 10% aqueous THF, which gave an amorphous solid (90%): i.r. (KBr) 3500—3200, 1690, and 1650 cm^{-1}; i.r. (CCl$_4$) 3050, 1690, and 1640 cm^{-1}. The i.r. data suggest that hydrates (**15**) and/or (**16**) were produced but that they exist in the amino-ketone form (**15b**) and/or (**16b**) in CCl$_4$, in contrast with 3-hydroxy-4-azahomoadamantane, the hydrate of (**4**);[5,9] this could be ascribed to the strain energy differences between 4-azahomoadamantane and azadihomoadamantanes.[10] Purification of the crude hydrate on an alumina column and/or sublimation were unsuccessful because of difficult separations and decomposition. Purification on a silica gel column after acetylation (acetic anhydride–pyridine or acetyl chloride–5% aqueous NaOH–CHCl$_3$) yielded the acetylamino-ketone (**17**) as an oil (45—50%). The shown structure was supported by the spectral data and was confirmed by an independent synthesis *via* (**19**) and (**20**) from (**18**) [45·6% from (**18**)]. These hydration and acetylation studies suggest that the imine (**7**) is inert even towards water under the examined conditions.‡

All of the above observations (Scheme) may be rationalised by the relative reactivity differences of the bridgehead imines (**7**) and (**8**) as well as by their modest reactivity to nucleophiles compared with the imines (**2**)—(**5**). Thus, the azide (**6**) undergoes facile photo-ring expansion to afford (**7**) and (**8**) in statistical ratio in contrast with the recently reported AlCl$_3$-catalysed decomposition,[11] which gave exclusively 1-adamantylcarbinyl derivatives *via* ring-contraction after the loss of the azido-group.

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‡ The imine (**7**) should be more stable (less reactive) than (**8**) on the basis of Wiseman's stability criterion (ref. 1) because (**7**) involves the *trans*-1-azacyclo-oct-1-ene moiety, while (**8**) involves the *trans*-1-azacyclohept-1-ene moiety.

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