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An Azidopiperideine → Dihydrodiazepine Ring Expansion of the Fluorocarbon Class: Synthesis of Perfluoro-(1,4-dimethyl-2,3-diazacyclohepta-1,3-diene) *via* Thermolysis of Perfluoro-(6-azido-2,6-dimethyl-1-azacyclohexene)

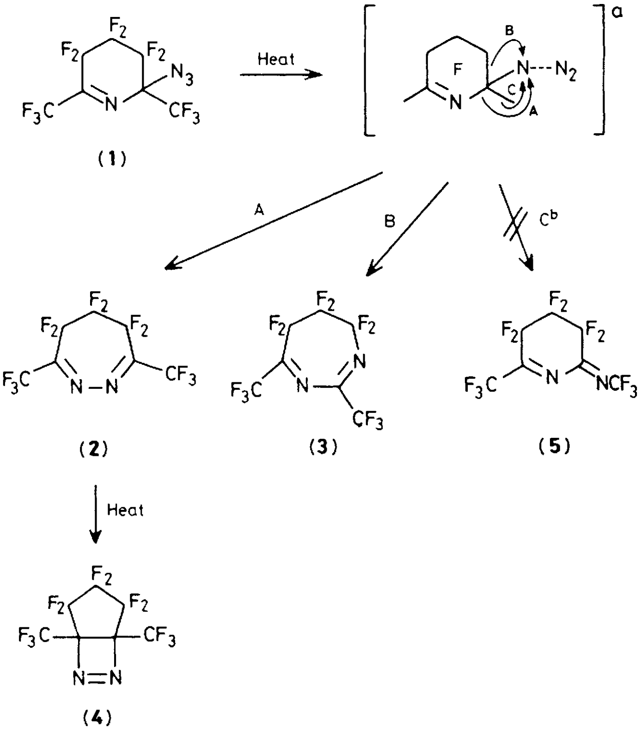
Mohammad Abed-Rabboh, Ronald E. Banks,* and Brian Beagley
Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.

Flow pyrolysis of perfluoro-(6-azido-2,6-dimethyl-1-azacyclohexene) at *ca.* 380 °C and 1 mmHg yields perfluoro-(1,4-dimethyl-2,3-diazacyclohepta-1,3-diene) (mainly) plus its isomers perfluoro-(1,5-dimethyl-6,7-diazabicyclo[3.2.0]hept-6-ene) and perfluoro-(2,4-dimethyl-1,3-diazacyclohepta-1,3-diene); the molecular geometry of the first of these products has been determined by gas-phase electron diffraction methods.

It is well established that expansion of aromatic or cycloaliphatic skeletons can be triggered by thermolysis or photolysis of azido derivatives of hydrocarbon systems.[1] By contrast, knowledge of azide-based ring expansions in fluorocarbon chemistry is confined to a single example: thermolysis of azidopentafluorobenzene, which yields perfluoro-2,7′-diazaheptafulvalene.[2] We now report the first ring expansion involving a cyclic perfluorinated azide in which the N_3 moiety is attached to sp^3-hybridized carbon, namely perfluoro-(6-azido-2,6-dimethyl-1-azacyclohexene) (**1**), prepared by nucleophilic azidation of perfluoro-(2,6-dimethyl-1-azacyclohexene).[3]

Flow pyrolysis of compound (**1**) in silica at *ca.* 380 °C and 1 mmHg† converted it completely into a *ca.* 4 : 1 : 1 liquid mixture (80% yield) of perfluoro-(1,4-dimethyl-2,3-diazacyclohepta-1,3-diene) (**2**), perfluoro-(2,4-dimethyl-1,3-diazacyclohepta-1,3-diene) (**3**), and perfluoro-(1,5-dimethyl-6,7-diazabicyclo[3.2.0]hept-6-ene) (**4**) plus nitrogen, trifluoroacetonitrile, perfluorocyclopropane, at least nine unidentified fluorocarbons, and traces of silicon tetrafluoride. G.l.c. was used to isolate a pure sample of the 5,6-dihydro-4*H*-1,2-diazepine (**2**) and an equimolar mixture of its isomers (**3**) and (**4**); the latter was shaken with aqueous sodium hydroxide, which, as expected, removed the 6,7-dihydro-5*H*-1,3-diazepine (**3**) but did not affect the bicyclic dihydro-1,2-diazete (**4**).

The dihydrodiazepines (**2**) and (**3**) are the two possible products arising from ring expansion brought about by forcing



Scheme 1. [a] Attempts are being made to determine if a trappable nitrene is involved.[6] [b] No evidence in support of this migratory mode has been found yet.

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† Tube size: 73 × 1.5 cm; heated length: 60 cm; azide flow-rate: 10 mmol h^{-1}. No decomposition and incomplete conversion, respectively, occurred at 200 and 300 °C.

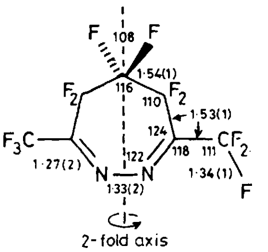

Figure 1. Molecular geometry of perfluoro-(1,4-dimethyl-2,3-diazacyclohepta-1,3-diene) (**2**): bond lengths in Å (1 Å = 10^{-10} m; e.s.d. in parentheses); bond angles in degrees (e.s.d. *ca.* 1°); torsion angle CNNC = 52(1)°.

the azido group to eject nitrogen (Scheme 1, pathways A and B); no evidence has been found yet to support the occurrence of migration of the trifluoromethyl group at the 6-position to the *exo*-nitrogen terminus [→ (**5**); pathway C]. Thermal electrocyclization of the 4*H*-isomer (**2**) provides an obvious route to the dihydrodiazete; and this is consistent with the observation that flow pyrolysis of the diazepine (**2**) at 580—590 °C and *ca.* 1 mmHg in silica yields the expected product of nitrogen extrusion from the diazetine, namely perfluoro-(1,2-dimethylcyclopentene), in addition to trifluoroacetonitrile (and unidentified fluorocarbons) arising from homolysis of the azine-type N–N link in the starting material (**2**) followed by β-C–C fission.

The structures of the new heterocycles (**2**—**4**) were established by standard procedures, namely elemental analysis (C, F, N) of the 1 : 1 mixture of compounds (**3**) and (**4**), and of compound (**2**), and spectroscopic [i.r., n.m.r. (^{19}F and ^{13}C), and mass] examination of (**3**) + (**4**), (**4**) alone, and (**2**). Compound (**2**) was also examined by electron diffraction, which established the molecular geometry shown in Figure 1 (refinements are still being made). The molecule adopts a twist-chair conformation with C_2 symmetry (like cycloheptane[4]) rather than assume the flatter C_s shape preferred by cyclohepta-1,3-diene.[5]

The products [CHF_3, CF_3CO_2H, CHF_2CHF_2, $HO_2C(CF_2)_2CO_2H$] formed *via* base-induced cleavage of compound (**3**) (see above; the hydrolysate was heated finally to 60 °C) are fully consistent with the structure deduced from analysis of the n.m.r. data for the mixture containing compound (**4**). Electron diffraction measurements on the dihydrodiazete (**4**) are in progress to determine the geometry of ring fusion and hence establish whether the electrocyclization postulated [(**2**) → (**4**)] falls into the conrotatory or disrotatory class; we intend to study in detail this bicyclic two-heteroatom version of butadiene ⇌ cyclobutene valence tautomerism.

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