A Novel Synthesis of Diareno-1,2-diazepines: Intramolecular Dehydrofluorination of 2,4,6-Trimethylphenylazo-derivatives of Fluoroaromatic Compounds

Adam C. Alty,[a] Ronald E. Banks,*[a] Brian R. Fishwick,[b] Robin G. Pritchard,[a] and A. Ronald Thompson[a]

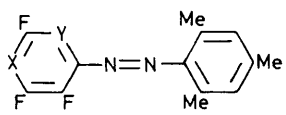
[a] *Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.*

[b] *Imperial Chemical Industries P.l.c., Organics Division, Hexagon House, Blackley, Manchester M9 3DA, U.K.*

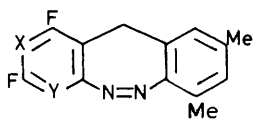
Formation of 1,2-diazepines *via* intramolecular elimination of hydrogen fluoride derived from methyl and fluorine substituents lying *ortho* to N=N linkages occurs when the azo-compounds 2,4,6-$Me_3C_6H_2N{=}NC_6F_5$, 2,4,6-$Me_3C_6H_2N{=}NC_6F_4CF_3$-4, and 4-(2,4,6-$Me_3C_6H_2N{=}N$)$C_5F_4N$ are heated in organic solvents; for example, 2,3,5,6-tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine cyclizes to give 1,3,4-trifluoro-7,9-dimethyl-11*H*-pyrido[4,3-*c*]benzo[1,2]diazepine, the molecular parameters of which have been determined by *X*-ray crystallography.

The literature pertaining to the chemistry of 1,2-diazepines, an area hailed recently as 'a new vista in heterocyclic chemistry,'[1] contains relatively little information on construction of the 11*H*-dibenzo[*c*,*f*][1,2]diazepine ring system[2] and apparently none on compounds of the latter type where one or both annelating moieties are themselves heterocyclic in nature. We report here a simple method for converting aminated monocyclic fluoroaromatic compounds into hitherto unknown 11*H*-diareno[*c*,*f*][1,2]diazepines, including compounds where one of the annelating species contains one or more nitrogen atoms. The method is unique because it involves azo-dyes as intermediates.

During studies on the diazotisation and azo-coupling of weakly basic aromatic amines in anhydrous hydrogen fluoride, the key discovery was made that recrystallization of the azo-compound (**1**) from glacial acetic acid converts it partly into the pyridobenzo-1,2-diazepine (**2**), a bright orange solid (m.p. 137—138 °C). This is not a 'clean' method (the by-products have not been identified yet), and a much better technique involves heating the azo-compound (**1**) in boiling mesitylene or *o*-dichlorobenzene; complete conversion of starting material into the 1,2-diazepine (**2**) occurs during 24 hours, and the latter can be isolated in at least 81% yield by dry-column flash chromatography. Similarly, the fluorinated azo-compounds (**3**) and (**5**) can be converted into the corresponding 1,2-diazepines (**4**) (m.p. 162—163 °C; 62% yield) and (**6**) (m.p. 113 °C; 89%). The azo-compounds (**1**), (**3**), and (**5**) are obtainable in at least 95, 33, and 93% yield, respectively, *via* addition of solid sodium nitrite to solutions of the appropriate amines Ar_FNH_2 (Ar_F = 4-C_5F_4N, C_6F_5, or 4-$CF_3C_6F_4$) in anhydrous hydrogen fluoride, followed by coupling of the resultant diazonium fluorides to mesitylene (*cf.* ref. 3). Work on solution-phase thermolysis of the corresponding pyrimidine compound (**7**) (obtained in 77% yield *via* diazotisation of 4-aminotrifluoropyrimidine in anhydrous HF) is still in progress; the 1,2-diazepine (**8**) is definitely formed but is accompanied by appreciable amounts of at least two other products which have not been identified yet.

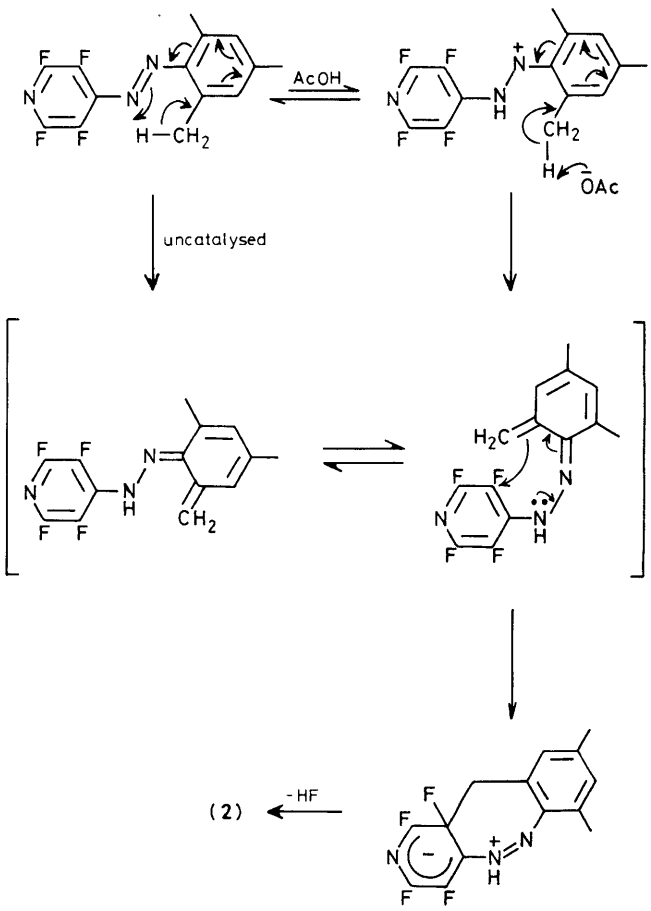


(**1**) X = N, Y = CF
(**3**) X = Y = CF
(**5**) X = CCF_3, Y = CF
(**7**) X = Y = N



(**2**) X = N, Y = CF
(**4**) X = Y = CF
(**6**) X = CCF_3, Y = CF
(**8**) X = Y = N

Whereas use of glacial acetic acid rather than mesitylene as the reaction medium speeds up the conversion of (**1**) into (**2**) considerably at 100 °C, neither 2,6-lutidine nor added radical scavengers appear to have any effect. *Tentatively*, then, we propose the ring-closure mechanism shown in Scheme 1, which clearly is of a type that rationalises the other azo → 1,2-diazepine conversions reported here. *X*-Ray analysis of the azo-compound (**1**) has revealed that its molecules adopt a perfectly planar *trans*-conformation in the crystalline state.[4] The corresponding 1,2-diazepine has also been subjected to *X*-ray analysis, the results of which (see below) confirmed the initial identification by a combination of elemental analysis, spectroscopic methods, and reductive cleavage of the diazene



Scheme 1

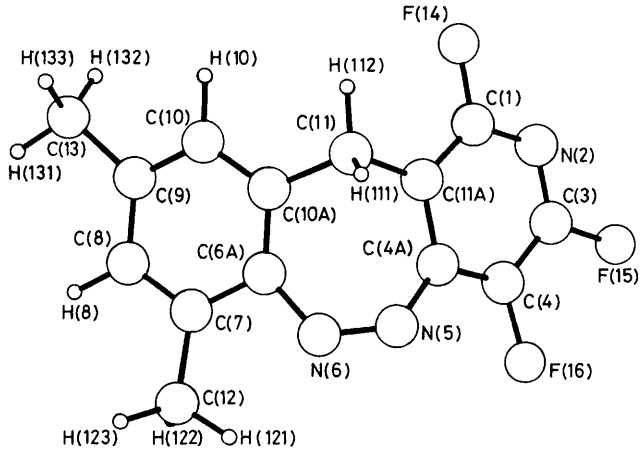


Figure 1. Geometry of the molecule of compound (**2**). Bond lengths (Å) averaged over three non-crystallographically related molecules are: C(1)–N(2), 1.29; C(1)–F(14), 1.35; N(2)–C(3), 1.28; C(3)–C(4), 1.35; C(3)–F(15), 1.35; C(4)–C(4A), 1.38; C(4)–F(16), 1.35; C(4A)–N(5), 1.43; N(5)–N(6), 1.26; N(6)–C(6A), 1.42; C(6A)–C(7), 1.39; C(6A)–C(10A), 1.38; C(7)–C(8), 1.38; C(7)–C(12), 1.52; C(8)–C(9), 1.38; C(9)–C(10), 1.37; C(9)–C(13), 1.52; C(10)–C(10A), 1.38; C(10A)–C(11), 1.51; C(11A)–C(1), 1.37; C(11A)–C(4A), 1.41; C(11A)–C(11), 1.48 (estimated standard deviations are 0.011—0.023 Å).

link. All the other new compounds mentioned here [(**3**)—(**8**)] possessed correct elemental compositions and spectroscopic properties [i.r., u.v., mass, and n.m.r. (^{1}H and ^{19}F)] consistent with the structures assigned.

Note that the surprising intramolecular condensation between a methyl group and an aromatic C–F moiety reported here finds analogy in the thermal conversion of acetophenone pentafluorophenylhydrazone and its heptafluoro-2-naphthyl counterpart into Fischer indole products, the mechanism of which remains undefined.[5]

Crystal data: compound (**2**): $C_{14}H_{10}F_3N_3$, monoclinic, space group *Cc*, $a = 20.678(6)$, $b = 12.590(5)$, $c = 15.686(6)$ Å, $\beta = 114.20(5)°$, $Z = 12$. Intensities were measured with a CAD 4 diffractometer for the range $0.05 < \sin\theta/\lambda < 0.6$ Å^{-1}. The structure was solved using MULTAN 80[6] and refined by least squares (SHELX[7]) to $R = 0.072$ for 1349 reflections having $F > 3\sigma(F)$. A total of 339 parameters were refined, all vibrational parameters being isotropic except for those of fluorine, which were treated anisotropically.†

Each molecule (Figure 1) comprises two planar units intersecting at an angle of 117° along a line joining C(11) to the mid-point of bond N(5)–N(6). Three molecules stack with nearly parallel aromatic rings at intervals of *b*/3 to form the asymmetric unit. Although one in every three molecules has undergone a two-fold rotation about the *b* direction, the pseudo-repeat of *b*/3 severely reduced the number of $k \neq 3n$ reflections and necessitated tying chemically equivalent bonds in the three independent molecules by constrained least-squares refinement. The resulting bond lengths agree well with published values.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.