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REACTIONS INVOLVING FLUORIDE ION. PART 34. A NOVEL RING CONTRACTION*

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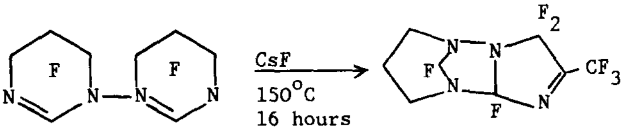
SUMMARY

The CsF-catalysed isomerisation of perfluoro-1,1'-bis-1,3-diazacyclohex-2-enyl (1) in the absence of solvent gave perfluoro-4-methyl-1,2,5,7-tetraazatricyclo[3.3.1.$0^{2.6}$]undec-4-ene (2) via intramolecular 1,3-attack at a saturated position in an intermediate nitrogen anion.

RESULTS AND DISCUSSION

The reaction of fluorinated di-imines with fluoride ion to give isomerisation and oligomerisation reactions via nitrogen anion intermediates is now established [1,2].

The novel di-imine, perfluoro-1,1'-bis-1,3-cyclohex-2-enyl (1) may be prepared in high yield by fluorination of tetrafluoropyrimidine [3] by cobalt trifluoride and we now find that (1) reacts with caesium fluoride, in the absence of solvent at 150°C, to give a product that has been identified as perfluoro-4-methyl-1,2,5,7-tetraazatricyclo[3.3.1.$0^{2.6}$]undec-4-ene (2).



(1)

(2) (42%)

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*Preliminary results presented by one of us (C.D.H.) at E.S.O.C. (IV), Aix-en-Provence, France, 2-6 September 1985.

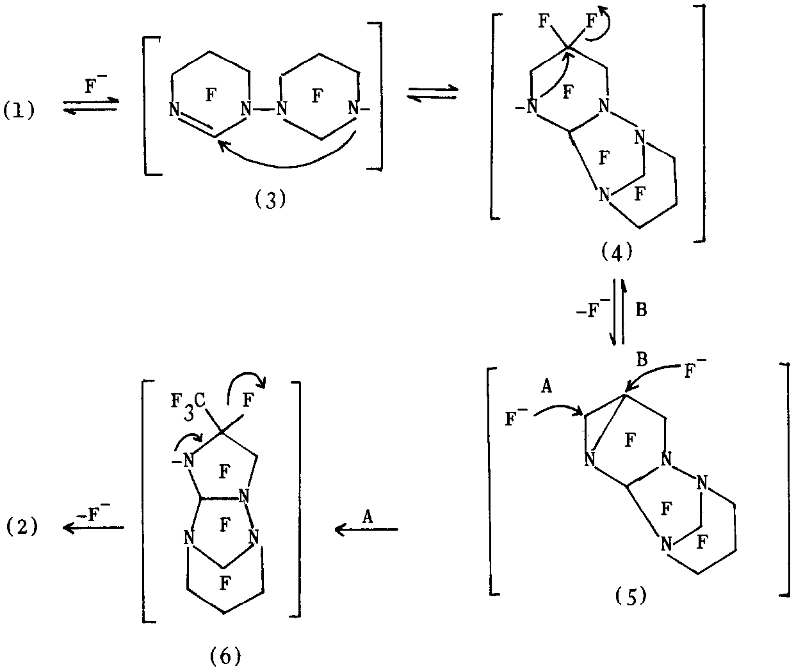
Part 33. R.D. Chambers, C.D. Hewitt, M.J. Silvester and E. Klauke, J. Fluorine Chem., 32 (1986) 389.

The structure of (2) was deduced from examination of spectroscopic data; the parent ion in the mass spectrum (EI, CI and negative ion) and elemental analysis demonstrates that (2) is isomeric with the starting material (1) and a single absorption in the infrared spectrum at 1720 cm^{-1} indicates only one unsaturated site. ^{19}F n.m.r. displays a series of AB signals between 89 and 118 p.p.m (intensity 8), together with a singlet at 127.1 p.p.m. (Int. 2), showing that (2) contains five CF_2 groups. The presence of a singlet at 107.5 p.p.m. (Int. 1) is consistent with a 'tertiary' fluorine atom shifted downfield by the influence of adjacent nitrogen atoms. The remaining signal at 60.5 p.p.m. (Int. 3) is characteristic of a CF_3 group attached to an unsaturated site. The ^{13}C n.m.r. spectrum is very complex due to carbon-fluorine coupling but displays a quartet at 117.2 p.p.m., characteristic of CF_3 and a triplet at 147.1 p.p.m. characteristic of sp^2 hybridized carbon that is not bonded directly to fluorine. The presence of a CF_3 group is a clear indication that ring contraction has taken place during the reaction and the absence of appropriate signals in the n.m.r. spectra indicate that there are no imino- or vinyl-groups attached to fluorine present, thus leaving (2) as the only reasonable structure consistent with the observed data and the structure of the starting material (1).

The proposed mechanism (see Scheme) for this novel isomerisation involves internal nucleophilic attack at a saturated position, i.e. (4) to (5). The first stages of the isomerisation are obvious in that reaction must proceed via initial addition of fluoride ion to (1), giving a nitrogen anion (3), followed by intramolecular nucleophilic addition to a double bond, to give (4). More controversial, however, is the novel ring contraction of (4) to give (5), apparently via internal attack at a saturated position in a step reminiscent of the Favorskii rearrangement. Further attack of fluoride ion could then occur at position A or B in intermediate (5); attack at B would simply cause return to (4), whereas attack at A gives nitrogen anion (6), from which, elimination of fluoride ion gives the observed product (2).

EXPERIMENTAL

Compound (1) (3.3 g., 7.9 m.mol) was transferred under vacuum to a Carius tube (volume 10 ml.) containing dry CsF (~0.5 g.). This was sealed under high vacuum and then heated to 150°C for 16 h. with vigorous shaking. Volatile material was transferred under vacuum to a trap cooled in liquid air and the resultant liquid (2.3 g.) was shown by g.l.c. (Column A* at 80°C) to contain two components. Separation by preparative scale g.l.c. gave (1) and perfluoro-4-methyl-1,2,5,7-tetraazatricyclo-$[3.3.1.0^{2.6}]$undec-4-ene (nc) (2) (42%): (Found: C, 23.0; F, 64.0; N, 13.2%. $C_8F_{14}N_4$ requires C, 23.0; F, 63.6; N, 13.4%).



Reaction Scheme

REFERENCES

1 R.D. Chambers, Fluorine in Organic Chemistry, Wiley-Interscience, New York, 1973 and references contained.

2 R.N. Barnes, R.D. Chambers, M.J. Silvester and C.D. Hewitt, J. Fluorine Chem., 24 (1984) 211.

3 R.D. Chambers, D.T. Clark, T.F. Holmes, W.K.R. Musgrave and I. Ritchie, J.C.S. Perkin 1 (1974) 114.

4 Column A: 20% Diisodecylphthalate on Chromosorb P.

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*Column A: 20% Diisodecylphthalate on Chromosorb P.