Journal of Fluorine Chemistry, *39* (1988) 227–233

Received: October 5, 1987; accepted: January 15, 1988

FLUOROCYCLOHEXANES. PART XVII. DEHYDROFLUORINATIONS OF THE *CIS* AND THE *TRANS* ISOMERS OF 2*H*-1-(DIFLUOROMETHYL)DECAFLUOROCYCLOHEXANE

JOHN BAILEY, RAYMOND G. PLEVEY and JOHN COLIN TATLOW*

Chemistry Department, The University, P.O.Box 363, Birmingham, B15 2TT (UK)

SUMMARY

2*H*-1-(Difluoromethyl)octafluorocyclohex-1-ene (I) and cobalt trifluoride at 165 °C afforded 2*H*-1-(trifluoromethyl)octafluorocyclohex-1-ene (IV) and four decafluorocyclohexane derivatives: the *cis* (III), and *trans* (V), -2*H*-1-(trifluoromethyl)- ; the *cis* (VII), and *trans* (VI), 2*H*-1-(difluoromethyl) compounds. Dehydrofluorination of VII, using aqueous potassium hydroxide, gave only one alkene, 1-(difluoromethyl)nonafluorocyclohex-1-ene (VIII). In a slower reaction VI afforded two alkenes, mainly VIII, but also an isomer, 1-(difluoromethyl)nonafluorocyclohex-2-ene (IX) (ratio 2:1).

INTRODUCTION

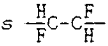
Polyfluorocyclohexanes provide a fertile field for the study of alkene-forming elimination reactions by dehydrofluorination [1]:- $>CH-CF< + OH^- \Rightarrow >C=C< + H_2O + F^-$. Major factors controlling these processes are the differing strengths of the adjacent C-H and C-F bonds that can rupture, with effective loss of HF, and generation of the ethylenic bond. The molecular geometry of the cyclohexane ring is also involved; whether potential leaving groups are carried on axial or equatorial positions will significantly alter reaction rates, and may affect the range of products obtained. Thus, *cis* and *trans* members of a stereoisomeric pair can differ significantly in their behaviour during dehydrofluorination [cf 2,3]. In contrast, amongst the polyfluoro -cyclopentanes [4] and -cycloheptanes [5], dehydrofluorinations of *cis* and *trans* stereoisomers do not usually show significant variations.

---

*Present Address: 30 Grassmoor Road, Kings Norton, Birmingham, B38 8BP (UK)

0022-1139/88/$3.50

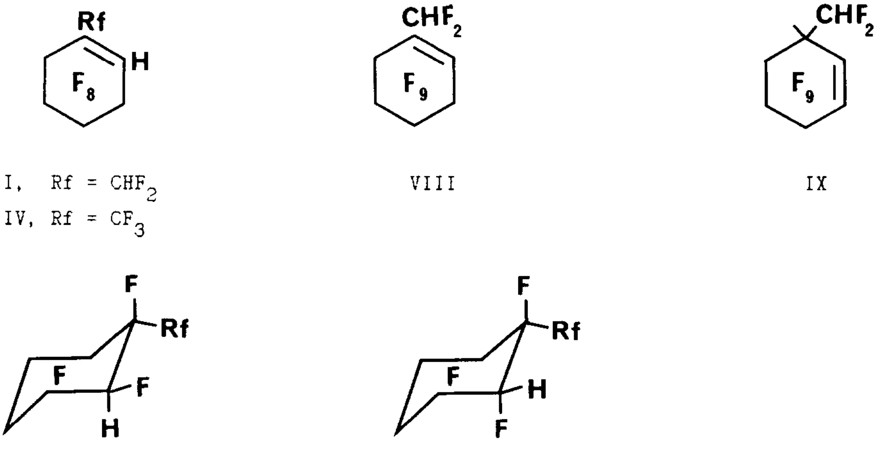
These different reactivities arise because the particular conformations from each ring system that have maximum stability are dissimilar [6]; hence H and F are in different relative positions. Heterogeneous reaction media (aqueous base) have been used in the dehydrofluorinations concerned, thereby minimizing nucleophilic attack on the polyfluorocycloalkene products, and it appears that concerted bimolecular mechanisms apply. If discrete carbanion intermediates were formed, reactivities should be more uniform than the experimental findings, and uptakes of deuterium should be more pronounced [7].

As a rough guide, the facile dehydrofluorinations (for similar C-H and C-F bonds) seem to be those of compounds having molecular geometries related to those of the respective cycloalkene products. This arises when the residual substituents (which become vinylic), and the two ring carbons carrying them, come close to lying in one plane, and hence are positioned reasonably correctly for product formation. A *syn* coplanar structure is present in those fluoro-cyclopentanes and -cycloheptanes having *trans*  $\overset{H}{\underset{F}{-}}C\text{-}C\overset{F}{\underset{H}{-}}$ moieties. *Anti* coplanar arrangements of potential leaving groups are achieved from the corresponding *cis* isomers without great difficulty, both carbocyclic systems being quite flexible (conformers are easily interconverted [6]).

The 6-membered ring is more restricted conformationally than are the 5- and the 7-membered ones. Assuming chair forms, *anti* periplanar arrangements of H and F, leading to *trans* eliminations, are readily achievable when both substituents are axial (a *cis* 1*H*,2*H* isomer). If either H or F is equatorial, however, both *syn* and *anti* coplanar geometries are unlikely. Probably, other conformations, eg boat forms, must be assumed, or carbanions are involved.

Polyfluoro(alkylcyclohexanes) have particular features of interest. A bulky group such as trifluoromethyl will always take up an equatorial position, (if only F and H are present also). One stereoisomer of a 2*H* -compound (See Scheme; formulae III, V) will therefore have an equatorial H, and the other an axial one, and their dehydrofluorinations should show differences. However, when compounds III and V were dehydrofluorinated [8], the influence of the stereochemistry could not be demonstrated very satisfactorily.

The more readily available *cis* isomer (III) was dehydrofluorinated easily by aqueous KOH, but the product, 1-trifluoromethylnonafluorocyclohex-1-ene, itself suffered nucleophilic attack in the medium. Milder conditions limited this secondary reaction, but the *trans* isomer (V) was more resistant to HF loss, and little of it was available. Accordingly, dehydrofluorination was effected by passage over sodium fluoride at <u>ca</u> 350 °C. Isomer V reacted significantly more slowly than did III, but the only product found from each



I, Rf = CHF_2
IV, Rf = CF_3

VIII

IX

III, Rf = CF_3
VII, Rf = CHF_2

V, Rf = CF_3
VI, Rf = CHF_2

SCHEME

was 1-trifluoromethylnonafluorocyclohex-1-ene. However, the other possible product, the isomeric -2-ene, could not be obtained even from the positional isomers of III and V, and this left doubts about its stability.

Another test with this type of compound became possible with the isolation [9] of 2*H* -1-(difluoromethyl)octafluorocyclohex-1-ene (I), a product of the fluorination of toluene by potassium tetrafluorocobaltate[III]. Cobalt trifluoride will usually add fluorine quite readily across such >C=C< bonds, and with no great stereochemical selectivity [10], so that compounds analogous to III and V became potentially available.

RESULTS AND DISCUSSION

It was anticipated that the major reaction to occur, when I was passed over cobalt trifluoride at *ca* 150 °C, would be addition of fluorine across the double bond, with little replacement of either hydrogen substituent. The desired adducts were formed optimally at 165 °C, but comprised only half of the product mixture. The compounds formed were perfluoromethylcyclohexane (II), 2*H* -1-(trifluoromethyl)/- (III), and 2*H* /-1-(trifluoromethyl)- decafluorocyclohexane (V), 2*H* -1-(trifluoromethyl)octafluorocyclohex-1-ene (IV), 2*H* /-1-(difluoromethyl)- (VI), and 2*H* -1-(difluoromethyl)/- decafluorocyclohexane (VII), besides some unchanged I. The recoveries of the products were as follows (molar %):- I, 1.6; II, 2.7; III, 5.5; IV, 19.2; V, 2.5; VI, 13.9; VII, 11.6.

Compounds III and V [8], and IV [9] were known. The structures of VI and VII followed from analytical and spectroscopic data. In each of their ^{1}H and ^{19}F nmr spectra, there were typical peaks for a $-CHF_2$, and for a >CHF group; there was also a characteristic tertiary fluorine peak. VI had its >CHF fluorine peak at 213 ppm, whilst for VII it was at 233: these are the expected values [11] for peaks from respectively an axial, and an equatorial fluorine substituent in this type of structure. Hence, compound VI was the *trans* -stereoisomer (eq-CHF_2,eq-H), and VII the *cis* (eq-CHF_2, ax-H).

This fluorination reaction followed a rather unusual course: it would appear that the hydrogen of the difluoromethyl group is more readily replaced by fluorine than is usual, presumably because this group is carried in an allylic position. This replacement, and addition of fluorine to the double bond, went at similar rates. In contrast, replacement of the vinylic H was a much slower process, as witnessed by the failure to find either (difluoromethyl)-nonafluorocyclohexene, or -undecafluorocyclohexane, or a (trifluoromethyl)nonafluorocyclohexene among the products. Fortunately, the addition to the double bond was not stereoselective [cf 10]; enough of both VI and VII could be made to study the point at issue.

Compound VII, being the *cis* -isomer, had an axial hydrogen adjacent to an axial tertiary fluorine: fluorine substituents of this type are usually eliminated in preference to those in $>CF_2$ groups [7]. The expectation was, therefore, that treatment of VII with aqueous potassium hydroxide would give 1-(difluoromethyl)nonafluorocyclohex-1-ene (VIII) under relatively mild conditions. This corresponded with the experimental result, since VIII and recovered VII were the only compounds present: alkene VIII was known [12,13].

In contrast, dehydrofluorination of the *trans* -isomer (VI) was significantly slower. A longer reaction time afforded a three-component mixture, the major one being VI. The others, in roughly 2:1 ratio, were alkene VIII, and a new alkene IX. This analysed as C_7HF_{11}, but was not the known [9] 3-ene isomer of VIII. That it was the other possible product, 1-(difluoromethyl)nonafluorocyclohex-2-ene (IX) was confirmed spectroscopically. The ir spectrum showed a typical >CF=CF< band at 1740 cm^{-1}, whilst the ^{19}F nmr spectrum had two peaks due to vinylic fluorine, and one from tertiary F, at lower field than the corresponding peak in the spectrum of the 3-ene [9].

This result is entirely in accord with our previous results on dehydrofluorinations [cf 1-3, 7, 14]. Still uncertain, however, is whether the non-appearance of the trifluoromethyl analogue of IX in the earlier work [8] was due to instability, or to its failure to form under these conditions.

The hydrogen of the difluoromethyl group was not detectably involved in these reactions, no exocyclic alkenes or dienes being found. This is not so surprising, in view of the known stability [15, 16], towards elimination, of acyclic structures of this type, related to their low carbon acidities [17].

EXPERIMENTAL

The general techniques and apparatus used have been described before [13].

Fluorination of 2 H*-1-(Difluoromethyl)octafluorocyclohex-1-ene (I)*

The alkene I, in a stream of nitrogen (1.5 lh^{-1}), was passed over CoF$_3$ in Reactor 2 held at 165 °C. From four runs, I (25.0 g) gave a mixture of seven components (24.0 g) after work-up as usual. Preparative glc (D, 80°, 40) gave the following products:- (i) (0.85 g), perfluoromethylcyclohexane (II); (ii) (1.65 g), 2*H* -1-(trifluoromethyl)/-decafluorocyclohexane (III, *cis*) [8]; (iii) (5.10 g), 2*H* -1-(trifluoromethyl)octafluorocyclohex-1-ene ((IV) [9]; (iv) (0.75 g), 2*H* /-1-(trifluoromethyl)decafluorocyclohexane (V, *trans*) [8]; (v) (3.95 g), 2*H* /-1-(difluoromethyl)decafluorocyclohexane (VI, *trans*); (vi) (3.30 g), 2*H* -1-(difluoromethyl)/-decafluorocyclohexane (VII, *cis*); (vii) (0.40 g), recovered starting material (I).
VI (nc) had b.p. 98 °C, M/e, 295 (M-19); ir ca 3000 (vw); (Found: C, 26.7; H, 0.8; F, 72.7. $C_7H_2F_{12}$ requires C, 26.8; H, 0.6; F, 72.6 %).
VII (nc) had b.p.102 °C, M/e, 295 (M-19); ir 2980 (w); (Found: C, 27.1; H, 0.8; F, 72.2 %).

Dehydrofluorination Reactions

The *cis* -isomer (VII). This (1.50 g), and a solution of potassium hydroxide (1.50 g) in water (3.0 cm^3), were stirred together magnetically at 80 °C. Monitoring by glc (B, 70°, 4.7) showed that reaction occurred progressively. After 30 minutes, work-up as usual gave a liquid (0.90 g). Glc separation of this (C1, 140°, 4.5) afforded:- (i) (0.40 g), 1-(difluoromethyl)nonafluorocyclohex-1-ene (VIII) [13]; (ii) (0.25 g), the recovered *cis* -2*H* -1-(difluoromethyl)/-isomer (VII).

The *trans* -isomer (VI). This (4.0 g) was stirred magnetically with a solution of potassium hydroxide (4.0 g) in water (8.0 cm^3) at 80 °C. After

30 minutes, much less reaction had occurred than with isomer VII, and heating was continued for 1 hour further. The product (2.40 g) was separated by glc (C1, 110°, 4.5) to give:- (i) (0.39 g), the 1-ene (VIII); (ii) (0.20 g), the 2-ene (IX); (iii) (1.00 g), recovered *trans* -isomer (VI). Fraction (ii) was 1-(difluoromethyl)nonafluorocyclohex-2-ene (IX) (nc); b.p. 90-91 °C; M/e, 294 (M); ir 1740 (m), 2990 (w); (Found: C, 28.3; H, 0.6; F, 71.1. C_7HF_{11} requires C, 28.6; H, 0.3; F, 71.1 %).

TABLE

NMR SPECTRA OF COMPOUNDS III, VI, VII, IX

b = broad, c = complex, d = doublet, m = multiplet, s = singlet, t = triplet

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
III	H	5.20	-	>CHF	d of m; J_{HF} = 44.4
	F	73.0	3	$-CF_3$	m
		130.0	2	$>CF_2$	m
		121.2;133.2	2	$>CF_2$	AB; J_{AB} = 333
		123.4;140.2	2	$>CF_2$	AB; J_{AB} = 289
		123.2;145.0	2	$>CF_2$	AB; J_{AB} = 285
		202.0	1	→CF	bs
		235.1	1	>CHF(eq)	d of m; J_{HF} = 44.4
VI	H	5.13	1	>CHF	d of m; J_{HF} = 43.2
		6.31	1	$-CHF_2$	t of d;J = 51.0,12.0
	F	115.7-144.4	8	$>CF_2$	series of cm
		137.1	2	$-CF_2H$	d; J = 51.0
		199.9	1	→CF	bs
		213.0	1	>CFH(ax)	d of m; J_{HF} = 43.2
VII	H	5.22	1	>CHF	d of m; J_{HF} = 45.1
		6.23	1	$-CHF_2$	t of d;J = 52.5,4.0
	F	120.1-147.9	10	$>CF_2$	series of cm
		199.7	1	→CF	s
		233.4	1	>CFH(eq)	d of m; J_{HF} = 45.1
IX	H	6.18	1	$-CHF_2$	t of d;J = 52.0,3.8
	F	107.7-137.8	8	$>CF_2$	series of cm
		141.0	1	-FC=	bs
		145.8	1	=CF-	bs
		170.9	1	→CF	bs

REFERENCES

1 Part XV of this Series; P. L. Coe, A. W. Mott and J. C. Tatlow, J. Fluorine Chem., <u>*20*</u> (1982) 167; also earlier papers cited therein.

2 R. P. Smith and J. C. Tatlow, J. Chem. Soc., (1957) 2505.

3 E. Nield, R. Stephens and J. C. Tatlow, J. Chem. Soc., (1959) 159.

4 J. Burdon, T. M. Hodgins, R. Stephens and J. C. Tatlow, J. Chem. Soc., (1965) 2382.

5 A. E. M. M. Khalil, R. Stephens and J. C. Tatlow, J. Fluorine Chem. <u>*22*</u> (1983) 31: D. J. Dodsworth, C. M. Jenkins, R. Stephens and J. C. Tatlow, ibid, <u>*24*</u> (1984) 41.

6 E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, 'Conformational Analysis,' Interscience, New York, (1962) Chapter 4.

7 D. Collins, R. Stephens and J. C. Tatlow, J. Fluorine Chem., <u>*32*</u> (1986) 213.

8 Part XVI of this Series; D. J. Alsop, J. Burdon, P. A. Carter, C. R. Patrick and J. C. Tatlow, J. Fluorine Chem., <u>*21*</u> (1982) 305.

9 J. Bailey, R. G. Plevey and J. C. Tatlow, J. Fluorine Chem., <u>39</u> (1988) 23.

10 A. Bergomi and J. Burdon, J. Chem. Soc., Perkin I, (1975) 2237.

11 J. Homer and L. F. Thomas, Trans. Farad. Soc., <u>*59*</u> (1963) 2431: A. Peake and L. F. Thomas, ibid., <u>*62*</u> (1966) 2980.

12 J. Riera and R. Stephens, Tetrahedron, <u>*22*</u> (1966) 2555.

13 J. Bailey, R. G. Plevey and J. C. Tatlow, J. Fluorine Chem., <u>*37*</u> (1987) 1.

14 S. F. Campbell, F. Lancashire, R. Stephens and J. C. Tatlow, Tetrahedron, <u>*23*</u> (1967) 4435.

15 R. N. Haszeldine, J. Chem. Soc., (1953) 3761.

16 G. B. Barlow, M. Stacey and J. C. Tatlow, J. Chem. Soc. (1955) 1749.

17 S. Andreades, J. Am. Chem. Soc., <u>*86*</u>, (1964) 2003.