Tetrahedron. Vol. 23, pp. 4435 to 4439. Pergamon Press Ltd. 1967. Printed in Great Britain

FLUOROCYCLOHEXANES—XII[1]

NOVEL ELIMINATION REACTIONS OF 1H,2-CHLORO/-DECAFLUOROCYCLOHEXANE AND 1H,2-CHLORO/-1-CHLORONONAFLUOROCYCLOHEXANE

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(*Received* 3 *March* 1967; *accepted for publication* 3 *April* 1967)

Abstract—The stereoisomeric 1H,2-chlorodeca—and 1H,1,2- dichlorononа—fluorocyclohexanes have been prepared and characterised. The dehydrohalogenations of 1H,2-chloro/-decafluoro—and 1H,2-chloro/1-chloro-nonafluoro—cyclohexane with aqueous alkali are unusual in that there appears to be a simultaneous operation of *anti*—and *syn*-elimination processes; some comments on possible mechanisms have been made.

THE replacement of chlorine by hydrogen in a chlorofluorocarbon using lithium aluminium hydride in diethyl ether is a well known reaction.[2,3] 1,2-Dichlorodecafluorocyclohexane gives 1H/2H- and 1H,2H/-decafluorocyclohexane.[4] We have found that use of a deficiency of lithium aluminium hydride with dichloro-compounds will produce substantial amounts of chloro-hydro-products. Thus, 1,2-dichlorodecafluorocyclohexane gave two chlorodecafluorocyclohexanes which were readily separated by gas chromatography, and were characterized by analysis and mass spectrometry. Further reduction with lithium aluminium hydride converted each isomer into a mixture of 1H/2H- and 1H,2H/-decafluorocyclohexane, showing that the reaction is not stereospecific. Dehydrohalogenation with aqueous potassium hydroxide at room temperature was used to allocate the stereochemistry of the two isomers. Under comparable conditions, the less volatile monochloride gave decafluorocyclohexene (III; X = F) as the sole product with no unchanged starting material, whereas only about 70% of the isomeric chloride was attacked to give largely 1-chlorononafluorocyclohexene (86%; IV; X = F) together with decafluorocyclohexene (14%; III; X = F). The first monochloride is therefore 1H/2-chlorodecafluorocyclohexane (II) or (II*; X = F) which can undergo anti-periplanar dehydrochlorination, and the second the 1H,2-chloro/-stereoisomer (I; X = F). From the latter the major unsaturated product will arise from the expected anti-periplanar dehydrofluorination but the formation of decafluorocyclohexene is of considerable interest in that it arises from groups that are synclinal in a chair conformation.

The chlorination of 1H-nonafluorocyclohexene gave *cis*- and *trans*-1H-1,2-dichlorononafluorocyclohexane which were separated by gas chromatography

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[1] Part XI. W. J. Feast and R. Stephens, *J. Chem. Soc.* 5493 (1965).

[2] J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.* 1251 (1952).

[3] J. Burdon, T. M. Hodgins, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.* 2382 (1965).

[4] R. P. Smith and J. C. Tatlow, *J. Chem. Soc.* 2505 (1957).

and characterized by analysis and mass spectrometry. The minor, more volatile, component and aqueous potassium hydroxide gave 1-chlorononafluorocyclohexene (IV; X = F) as the sole product, thus establishing its structure as 1H/2-chloro-1-chlorononafluorocyclohexane (II; X = Cl). The stereoisomeric chloride under identical conditions gave largely 1,2-dichloro-octafluorocyclohexene (82%; IV; X = Cl) by an anti-periplanar dehydrofluorination, but 1-chlorononafluorocyclohexene (18%; III; X = Cl) was also formed and this seems to be another example of a syn-clinal dehydrochlorination competing with an anti-periplanar dehydrofluorination.

It is unlikely that the sterically unfavourable dehydrochlorination which occurs in 1H,2-chloro/decafluorocyclohexane (I; X = F) and 1H,2-chloro/1-chlorononafluorocyclohexane (I; X = Cl) is an E2 process in a chair conformation I. A syn-clinal E2 process in a boat conformation VIII is a possibility,[5] since the general stereochemical situation is then similar to that in a cyclopentane from which such eliminations occur.[6] An alternative is an elimination *via* a carbanion V. Deuteriation experiments were therefore carried out and both 1H,2-chloro/-stereoisomers (I; X = F and Cl) were deuteriated by potassium hydroxide in deuterium oxide, as were undeca- and 1H/2H-deca-fluorocyclohexane.[†] 1H/2-Chlorodecafluorocyclohexane (II; X = F) was not detectably deuteriated under comparable conditions, like 1H,2H/-decafluorocyclohexane. The precise role of the carbanion (V; X = F or Cl) is not clear, however. Thus, as depicted in the figure, it could undergo a non-coplanar elimination of chloride ion (it is known[7] that non-coplanar eliminations from highly fluorinated carbanions can occur) to give (III; X = F or Cl), as well as the more likely coplanar elimination of fluoride ion to give IV. It could invert its configuration to give VII and equilibrate with the conformer VI, which could either lose chloride ion in a coplanar elimination to give III or reprotonate to II* (the mirror image of II) which gives III in an E2 process. Unfortunately, little is known at present about the configurational stability of polyfluoro-carbanions in systems of this type.

EXPERIMENTAL

Gas chromatography. Analytical work was carried out using a glass column 2 m × 4 mm diam packed with dinonyl phthalate-celite (1:2; unit A). Preparative scale separations were made using columns 488 cm × 75 mm (col. A), 488 cm × 35 mm (col. B), 200 cm × 30 mm (col. C) all with the same packing as unit A.

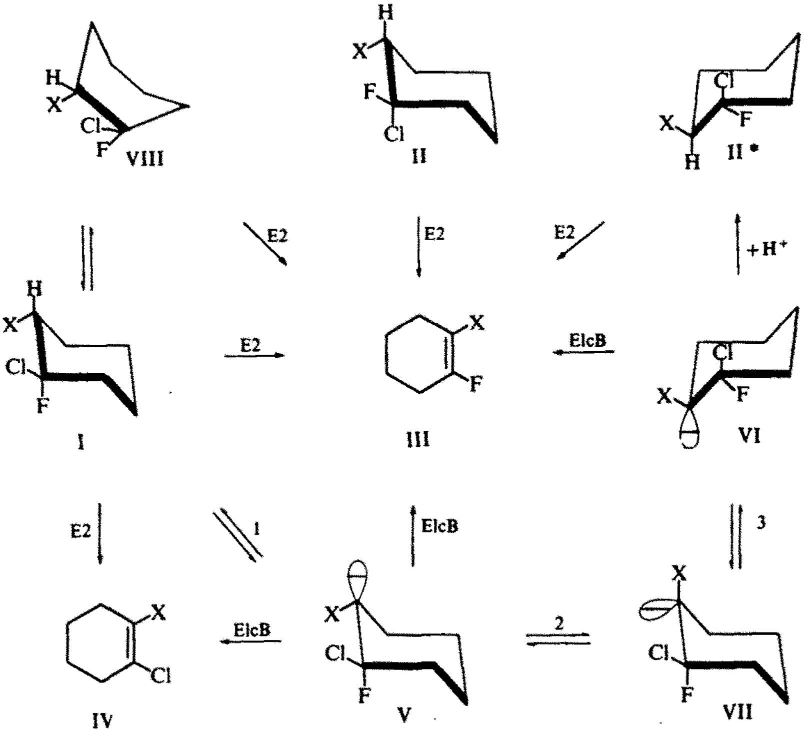
1H-2-*Chlorodecafluorocyclohexanes.* 1,2-Dichlorodecafluorocyclohexane (100·0 g) in ether (10 ml) was added during 4 hr to a well stirred suspension of LAH (7·0 g) in ether (400 ml) at room temp. The mixture was stirred at room temp for 2 hr and water (200 ml) was added followed by 2·5N HNO_3 (250 ml). The ether soln so obtained was separated, washed with water, dried ($MgSO_4$), filtered, evaporated through a Vigreaux column (1′) and the residue (90·0 g) separated by gas chromatography (col. A, 91°, N_2 44 l/hr) to give: (i) 1H/2H-decafluorocyclohexane[4] (8·2 g) with a correct IR spectrum; (ii) 1H,2-*chloro/decafluorocyclohexane* (30·1 g) b.p. 91° (Found: C, 23·9; H, 0·3. C_6HClF_{10} requires: C, 24·1; H, 0·3%), mass spectrometry gave a top mass peak of 298 (C_6HClF_{10}), (iii) 1H/2-*chloro-decafluorocyclohexane* (15·4 g), m.p. 19°

[†] In earlier work[6] no evidence for base-catalysed deuterium exhange was obtained using IR spectroscopy to analyse the reaction products; this technique was clearly too insensitive.

[5] D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.* 4828 (1963); J. Hine, R. D. Weimar, Jr., P. B. Langford, and O. B. Ramsay, *J. Am. Chem. Soc.* **88**, 5522 (1966).

[6] R. J. Heitzman, C. R. Patrick, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.* 281 (1963).

[7] S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron* 2997 (1965).



X = F or Cl
All unmarked substituents are fluorine.

b.p. 100°. (Found: C, 24·4; H, 0·4%), mass spectrometry gave a top mass peak of 298 (C_6HClF_{10}); (iv) 1H,2H/-decafluorocyclohexane[4] (25·0 g), with a correct IR spectrum.

1H-1,2-*Dichlorononafluorocyclohexanes.* 1H-Nonafluorocyclohexene (8·1 g) and Cl_2 (2·5 g) were kept in a sealed "Pyrex" tube irradiated with UV light for 24 hr at room temp and the product was washed with sodium metabisulphite soln, dried ($MgSO_4$), filtered and separated by gas chromatography (col. A, 100°, N_2 54 l./hr) to give: (i) 1H-nonafluorocyclohexene (0·4 g); 1H/2-*chloro-1-chlorononafluorocyclohexane* (0·5 g) b.p. 109° (Found: C, 22·7; H, 0·3. $C_6HCl_2F_9$ requires: C, 22·9; H, 0·3%), mass spectrometry gave a top mass peak of 314, ($C_6HCl_2F_9$); (iii) 1H,2-*chloro*/1-*chloro-nonafluorocyclohexane* (9·2 g) b.p. 115° (Found: C, 23·0; H, 0·3%), mass spectrometry gave a top mass peak of 314. Two other components were detected by analytical gas chromatography but could not be isolated on a preparative scale.

1H,2- Chloro/1-chlorononafluorocyclohexane (1·3 g) was refluxed with Zn dust (2·3 g) in dioxan (4 ml) for 4 hr. After cooling, the inorganic material was removed by filtration and 1H-nonafluorocyclohexene (0·5 g), with a correct IR spectrum, separated by gas chromatography (col. B, 90°, N_2 10 l./hr).

LAH reduction of 1H/2-*chlorodecafluorocyclohexane.* This compound (3·3 g) in ether (10 ml) was added during 40 min to a well stirred suspension of LAH (1·1 g) in ether (25 ml) at 0° and the stirring was continued for 3 hr. Water (20 ml) was then added to the mixture followed by 4N H_2SO_4 (50 ml) and the ether layer washed with water, dried ($MgSO_4$), filtered and distilled through a vacuum jacketed column (6″ × ½″) packed with glass helices. The residue (1·6 g) so obtained was shown by gas chromatography to contain, in addition to ether, two components with retention times identical to those of 1H/2H- and 1H,2H-/decafluorocyclohexane in the approx. ratio of 12:88, respectively, and a sample (80 µl., in two equal portions) was separated by semi-preparative scale gas chromatography (col. C, 78°, N_2 5·0 l./hr) to give: (i) ether; (ii) 1H/2H-decafluorocyclohexane; (iii) 1H,2H/-decafluorocyclohexane; all with correct IR spectra.

LAH reduction of 1H,2-*chloro/decafluorocyclohexane.* In the previously described manner, this compound (2·0 g) in ether (3 ml) and LAH (0·4 g) in ether (25 ml) at 0° gave a liquid product (1·5 g) which was shown by gas chromatography to contain ether and two other components with retention times identical to those

TABLE 1. PARTIAL DEUTERIATIONS

Polyfluorocycloalkane		KOH g	D_2O ml	Time hr	Temp. °C	Olefines g	Starting material g	%D in recovered starting material
1H/2-chlorodecafluorocyclohexane	(0·3 g)	0·3	1·0	0·33	18	0·1	0·1	0
1H,2-chloro/-decafluorocyclohexane	(1·7 g)	3·0	5·0	0·33	18	0·3	0·6	6
1H,2-chloro/-1-chloro-nonafluorocyclohexane	(2·8 g)	4·0	7·0	1	0	1·2	0·7	4
1H/2H-decafluorocyclohexane*	(5·0 g)	7·0	7·0	2	18	0·5	3·0	3
1H,2H/-decafluorocyclohexane*	(1·8 g)	3·0	3·0	0·01	18	~0·5	~0·6	0
1H-undecafluorocyclohexane	(5·0 g)	6·0	10·0	0·25	0	1·8	0·5	40

* With A. B. Clayton.

of 1H/2H- and 1H,2H/-decafluorocyclohexane in the approx. ratio of 17:83, respectively. A sample (80 µl., in two equal portions) was separated by semi-preparative scale gas chromatography (col. C, 76°, N_2 6·0 l./hr) to give: (i) ether; (ii) 1H/2H-decafluorocyclohexane; (iii) 1H,2H/-decafluorocyclohexane; all with correct IR spectra.

Dehydrohalogenations

1H/2-Chlorodecafluorocyclohexane (4·1 g) was shaken with 18N KOH (15 ml) in a sealed "Pyrex" tube at room temp for 14 hr and the organic layer separated, washed with water, dried ($MgSO_4$), filtered and distilled to give decafluorocyclohexene (3·2 g) with a correct IR spectrum; a very minor component was detected by analytical gas chromatography.

1H,2-Chloro/decafluorocyclohexane (4·0 g) was treated in precisely the same way as the *trans*-isomer and the product separated by gas chromatography (col. B, 90°, N_2 10 l./hr) to give: (i) decafluorocyclohexene (0·2 g) with a correct IR spectrum; (ii) 1-*chlorononafluorocyclohexene* (1·3 g) b.p. 80° (Found: C, 26·0; H, 0·1. C_6ClF_9 requires: C, 25·9%), ν max 1695 cm^{-1} (—CF=CCl—) with a consistent ^{19}F NMR spectrum;[8] this olefin (2·3 g), $KMnO_4$ (4·3 g) and acetone (60 ml) at 18° for 1 hr gave octafluoroadipic acid which was isolated as its dianilinium salt (1·6 g) m.p. 214° (cited[9] 214°); (iii) starting material (1·4 g) with a correct IR spectrum.

1H/2-Chloro-1-chlorononafluorocyclohexane (0·8 g) under the standard conditions gave only 1-chlorononafluorocyclohexene (0·4 g) with a correct IR spectrum.

1H,2-Chloro/1-chlorononafluorocyclohexane, (11·1 g) under the standard conditions, gave a liquid product which was separated by gas chromatography (col. A, 99°, N_2 60 l./hr) to give: (i) 1-chlorononafluorocyclohexene (1·8 g) with a correct IR spectrum; (ii) 1,2-dichloro-octafluorocyclohexene (8·1 g) b.p. 112° (cited[10] 113°). (Found: C, 24·3; H, 0·0 Calc. for $C_6Cl_2F_8$: C, 24·4%), ν max 1645 cm^{-1} (—CCl=CCl–); this olefin (3·0 g), $KMnO_4$ (5·1 g) and acetone (65 ml) at 18° for 1 hr gave octafluoroadipic acid which was isolated as its dianilinium salt (1·7 g) m.p. 215° (cited[9] 214°).

Partial deuteriations

General procedure. The fluoro-compound was shaken with soln of KOH in D_2O and when analytical gas chromatography indicated ca. 50% dehydrohalogenation the organic layer was separated by preparative scale gas chromatography (col. B) and the recovered starting material examined by mass spectrometry; the results are set out in the table.

Acknowledgements—The authors thank Dr. J. R. Majer for the mass spectral measurements and the D.S.I.R. for maintenance awards (to S.F.C. and F.L.).

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