

Received: March 26, 1981

REACTIONS INVOLVING FLUORIDE ION.

PART 24 [1]. SYNTHESSES FROM PERFLUOROCYCLOBUTENE

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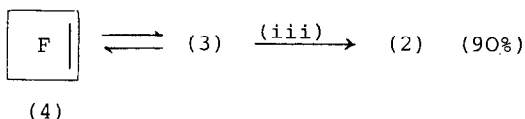
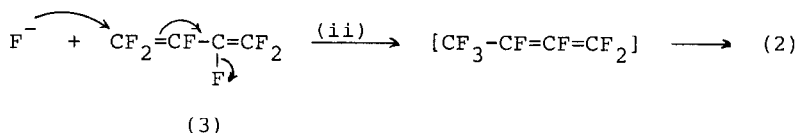
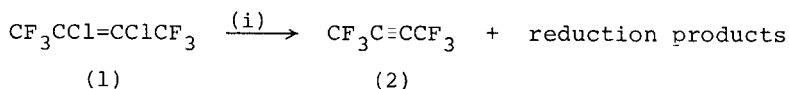
SUMMARY

Passage of perfluorocyclobutene, in a flow system, over caesium fluoride at 590-600° provides a synthesis of hexafluoro-2-butyne in high yield. In a similar process, using glass tubes, tricyclo[3.3.0.0<sup>2,6</sup>]octane and bicyclo[2.2.1]-2-heptene were obtained.

INTRODUCTION

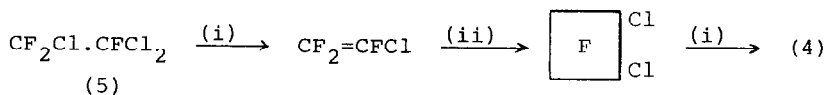
Hexafluorobut-2-yne (2) is a very reactive fluorinated system [2] and could be regarded as a 'building-block' for various other organic fluorine compounds. Although commercially available, it is very expensive and, normally, it is made from 2,3-dichlorohexafluorobut-2-ene (1), itself difficult to prepare without expertise in handling hydrogen fluoride. However, the published dechlorination procedures [3-5] are, unfortunately, accompanied by the formation of substantial amounts of reduction products.

## RESULTS AND DISCUSSION



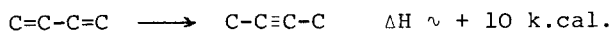
(i), Zn,  $(\text{CH}_3\text{CO})_2\text{O}$ ; (ii), CsF,  $100^\circ$ ; (iii), KF or CsF,  $590-600^\circ$ .

In 1961, in the course of his pioneering studies in fluoride-ion chemistry, Professor Miller and his co-workers [6] showed that perfluorobutadiene (3) is converted to perfluoro-2-butyne (2) by caesium fluoride at  $100^\circ$ . It is also well established that, at high temperatures, perfluorocyclobutene (4) is in equilibrium with perfluorobutadiene (3) [7]. Nevertheless, these observations have not previously been related but we now find that hexafluorobut-2-yne may be synthesised, in high yield, simply by passing (4) over potassium or caesium fluoride at high temperature; best results were obtained using potassium fluoride. Perfluorocyclobutene (4) can, of course, be obtained in high yield in the laboratory from trifluorotrichloroethane (5) [8], which is a large volume industrial chemical, and perfluoro-2-butyne (2) [9], b.p.  $-24.6^\circ$  [9], is easily separable from (4), b.p.  $3^\circ$  [9], by low-temperature distillation.



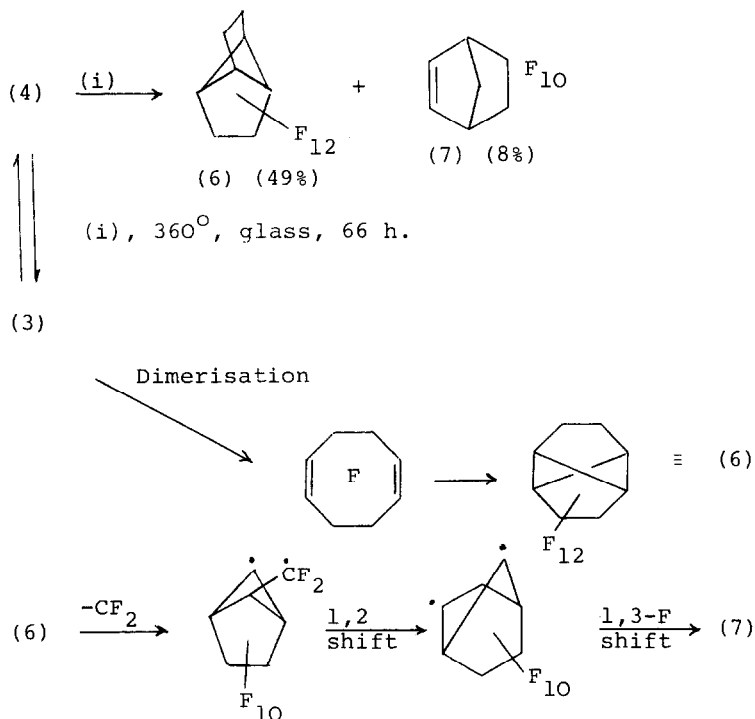
(i), Zn,  $\text{CH}_3\text{COOH}$ ; (ii), Autoclave  $200^\circ$ .

The fact that the equilibrium between (4) and (3) lies on the side of the ring system, whereas the reverse applies for the corresponding hydrocarbon compounds, is normally attributed to a destabilising interaction between electron-pairs on fluorine and the  $\pi$ -electrons of unsaturated carbon [10]. Such interactions are clearly fewer in (4) than (3). The conversion of a diene to a system containing a triple bond would not normally be expected, since a simple bond energy summation suggests that the process would be endothermic. However, the conversion of



(3) to (2) obviously removes all fluorine atoms from vinylic positions and, therefore, their corresponding electron-pair repulsions. It is this factor that must provide the driving force for the reaction. An optimum temperature of 590-600<sup>o</sup> was determined for the conversion of (4) to (2) and the reactions were carried out by passing (4), in a stream of dry nitrogen, over potassium fluoride contained in a silica tube. Yields of up to 90% with 95% recovery of material were observed. Higher temperatures gave increasing amounts of higher boiling material, which contained many components.

We have also investigated reaction of (4) with alkali-metal fluorides in static systems. In metal autoclaves, at high temperatures, extensive decomposition was observed but, using sealed glass tubes at 360<sup>o</sup>, with or without potassium fluoride, a mixture containing a number of components was obtained from which the unusual dimer (6) and perfluoro-norbornene (7) could be isolated. Compound (6) has been obtained previously by thermal dimerisation of perfluoro-1,3-butadiene at 150<sup>o</sup>, followed by prolonged heating of the dimer fraction at 200<sup>o</sup> [11], and identified by X-ray crystallography [12], although its spectral data has not been published. The F-19 n.m.r. spectrum of (6) does, in fact, show only two singlets, relative intensity 2:1, with the resonance corresponding to 'tertiary' fluorine occurring to especially high field. Perfluoro-norbornene (7) was identified by comparison of spectral data with those of an authentic sample [13]. A possible mechanism for production of (7) from (6) is shown in the Reaction Scheme.



Reaction Scheme

## EXPERIMENTAL

$^{19}\text{F}$  and  $^1\text{H}$  n.m.r. spectra were measured at  $40^{\circ}$ , using a Varian A56/60D spectrometer, with trichlorofluoromethane and tetramethylsilane as external reference. Upfield  $^{19}\text{F}$  shifts are quoted as positive. G.l.c. columns were packed with 30% silicone gum rubber SE30 (Col. O), or 20% di-isodecylphthalate on Chromosorb P.

Preparation of hexafluoro-2-butyne (2)

In the optimum experiment, perfluorocyclobutene (4) (33.3 g, 206 m.mol) was passed in a stream of dry nitrogen through a silica tube packed with anhydrous potassium fluoride pellets and

maintained at a temperature of 600°. The nitrogen flow rate was adjusted to give a contact time of approximately 30 secs. and the effluent gases collected in a series of traps, cooled in liquid air. After all of the starting material had passed through the tube, the traps were allowed to warm up to room temperature and the gaseous products (31.6 g) collected in a vessel fitted with a number of flexible reservoirs, leaving a multicomponent liquid (0.8 g) behind. The gas was analysed by g.l.c. and shown to consist of 94% hexafluoro-2-butyne and 6% perfluorocyclobutene (4). Low temperature distillation of the products from several such runs gave hexafluoro-2-butyne in ca. 99% purity.

In a similar experiment, (4) (62.4 g, 385 m.mol) was passed over potassium fluoride at 645° with a contact time of approximately 20 secs. The gaseous products (49.1 g) was shown to consist of a mixture of (2) and (4) in the ratio of 96:4. A yellow multicomponent liquid (7.9 g), was also collected but in view of the complexity of the mixture it was not investigated further.

#### Pyrolysis of perfluorocyclobutene (4)

A sample of (4) (6.1 g, 37.7 m.mol), contained in a Carius tube, was heated at ca. 360° for 66 h. Volatile material was transferred under vacuum to a cold trap to give, on warming, a gas (0.9 g) and a liquid (4.7 g). The gas was shown, by i.r. spectroscopy and g.l.c., to contain mainly (4), together with small amounts of silicon tetrafluoride and minor unidentified components. The liquid was shown by analytical scale g.l.c. (Col. O) to be a complex mixture of components, from which two were isolated by preparative-scale g.l.c. These were identified as perfluoronorbornene (7) [13], by comparison of spectroscopic data, and perfluorotricyclo[3.3.0.0<sup>2,6</sup>]octane (6) [11,12] m.p. 40°, b.p. 79° (lit. 40°, 80° respectively). Analysis: [Found: C, 29.7; F, 70.2%; M<sup>+</sup> 324. C<sub>8</sub>F<sub>12</sub> requires: C, 29.63; F, 70.37%; M, 324]; <sup>19</sup>Fδ, 129 (Int. 2), 220 (Int. 1) p.p.m.

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