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# Reactions involving fluoride ion
# Part 43 [1] Oligomerisations of hexafluoro-1,3-butadiene and -but-2-yne

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**Abstract**

Oligomerisation of hexafluoro-1,3-butadiene (**6**) and hexafluorobut-2-yne (**1**) occur with tetrakis(dimethylamino)ethene (**10**), in the absence of a solvent. Hydrogen-terminated oligomers are obtained but in the presence of pentafluoropyridine (**12**) or tetrafluoropyrimidine (**17**), simple trapping products are obtained. It is concluded that the polymerisation of **6** occurs by very rapid rearrangement to **1**, followed by polymerisation of the latter. 

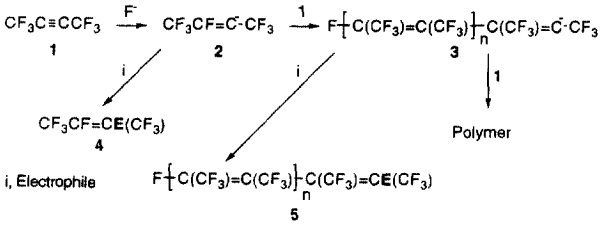
*Keywords:* Fluoride ion; Hexafluoro-1,3-butadiene; Hexafluorobut-2-yne

## 1. Introduction

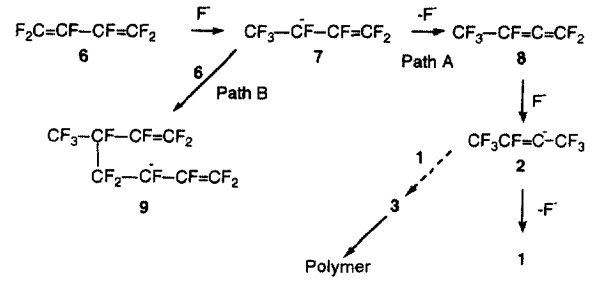
Fluoride ion reacts with hexafluorobut-2-yne (**1**) to give a polymer [2–4] in the absence of trapping agents but the intermediate ions, e.g., **2**, **3** can be trapped by some electrophiles including perfluorinated heterocycles [3] and bromine [5], Scheme 1, giving **4** and **5**, respectively.

More recently, it was established that reaction of hexafluoro-1,3-butadiene (**6**) with fluoride ion also gives a polymer [6] and it was proposed that this polymer is formed via an identical fluoride-ion induced rearrangement to hexafluorobut-2-yne (**1**), followed by the polymerisation of **1**, involving the process indicated in Scheme 2.

In the present study, we have set out to explore trapping experiments for the propagating anions in each polymerisation reaction, with a view to clarifying mechanism, Scheme 2, and we are also interested in the possibility of obtaining lower molecular-weight materials, terminated by heterocycles.




Scheme 1.




Scheme 2.

## 2. Results and discussion

In previous work in these laboratories [3], which involved trapping the propagating anions **2** and **3** derived from hexafluorobut-2-yne (**1**), we used caesium or potassium fluoride in an aprotic solvent, e.g., sulpholan, to generate the ions. Use of sulpholan, although effective, presents considerable difficulties for product isolation and the more recent use of tetrakis(dimethylamino)ethene (TDAE) (**10**), for the 'in-situ' generation of active fluoride, e.g., possibly **11**, Scheme 3, is a major practical advantage because reactions can often be conducted in the *absence of solvent*.

First, we confirmed earlier results by polymerising both hexafluorobut-2-yne (**1**) and hexafluoro-1,3-butadiene (**6**),

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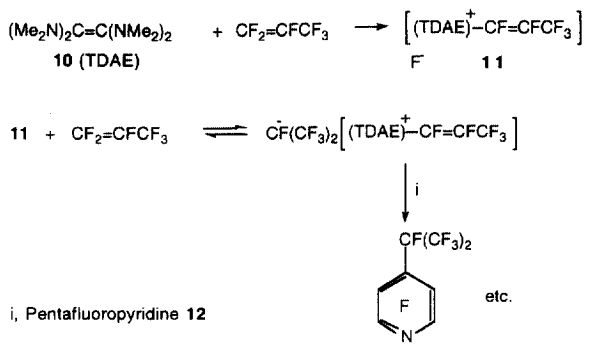
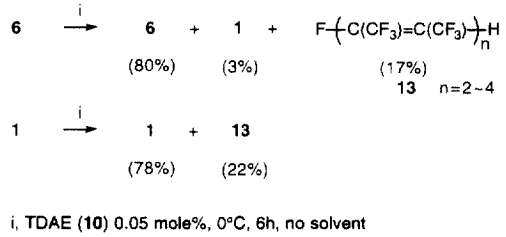



Scheme 3.




Scheme 4.

using caesium fluoride in sulpholan at 100°C, over 24 h. Each reaction produced a white polymer, insoluble in sulpholan, with a quantitative conversion of **1** but only 60% conversion of **6** under the same conditions. Solid-state $^{13}C$ and $^{19}F$ NMR spectra demonstrated that the polymers were identical. Each showed broad peaks $\delta_C$ at 120 ($CF_3$) and 133 (C=C) ppm and $\delta_F$ −61 ($CF_3$) ppm.

Reactions of both **6** and **1** with TDAE (**10**) did, indeed, occur in the absence of a solvent even at 0°C, in contrast to the use of caesium fluoride, where an aprotic solvent is essential to promote reaction to occur. Moreover, the use of TDAE without a solvent gave low molecular weight materials (**13**), derived from proton abstraction of the propagating anion (**3**) from the initiating system, Scheme 4.

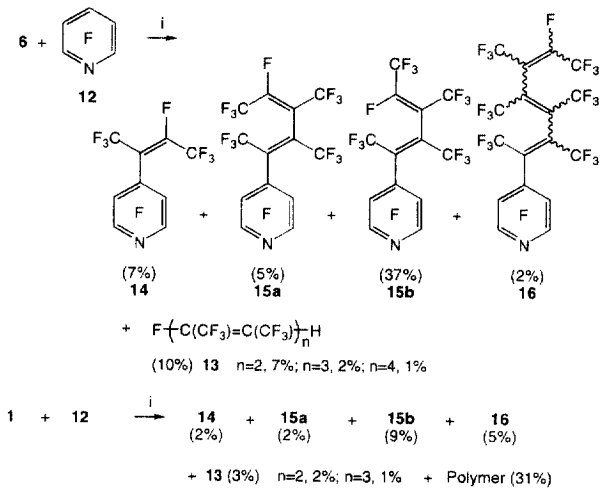
The structures of oligomers (**13**) were established by glc-ms and by $^{19}F$ NMR. Thus, TDAE (**10**) *without a solvent* is clearly a much more efficient initiating system than caesium fluoride *alone*, indeed, caesium fluoride in the absence of a solvent is quite ineffective for the generation of fluorocarbanions except at high temperatures [7]. Also, it is quite clear that the rearrangement process **6** to **1**, Scheme 2, is much more rapid than any reaction of **7** with hexafluoro-1,3-butadiene (**6**) or hexafluorobut-2-yne (**1**) since the products show no evidence of components derived from this process. Indeed, trace amounts of **1** were obtained in the product derived from **6**, Scheme 4.

Trapping experiments, using pentafluoropyridine (**12**) as electrophile, were conducted using **6** and **1**, using TDAE (**10**) to generate fluoride ion. Isolation of volatile products was therefore very easy from both systems, see Scheme 5.

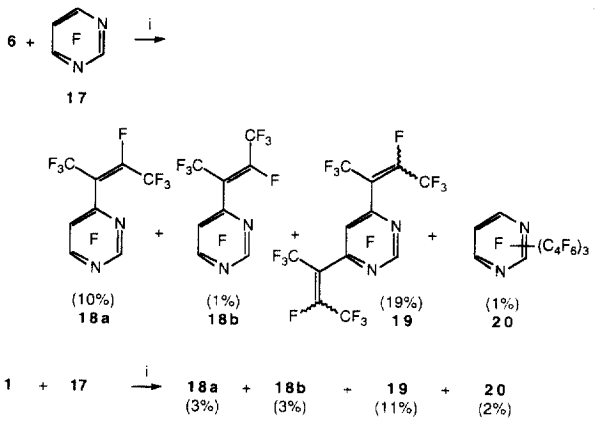
Using hexafluoro-1,3-butadiene (**6**), products **14–16** were isolated that derived entirely from trapping of the ions **2** and **3**, and oligomers **13**, which are also derived from **3**, were obtained. Surprisingly, reaction of hexafluorobut-2-yne (**1**) with pentafluoropyridine (**12**) gave insoluble polymer as the main product and relatively low yields of trapping products **14–16**. Clearly, in this case the pentafluoropyridine must act as a good solvent for **1**, in order to obtain a high enough concentration of **1** in solution, to produce polymers.

Tetrafluoropyrimidine (**17**) is a much more effective trapping agent for carbanions, being much more susceptible to nucleophilic aromatic substitution than pentafluoropyridine (**12**) [3]. Consequently, no polymer or even oligomers (**13**) were observed with either **1** or **6**, in reactions carried out in the presence of **17** at room temperature, where both **1** and **6** were in the gaseous state. The products are shown in Scheme 6, and a relatively low conversion of starting materials was observed, although the conversion could be improved by using higher temperatures.

Vacuum transfer of the products left a residue derived from the TDAE (**10**) but the $^{19}F$ NMR spectrum of this material showed very little residual fluorine indicating that negligibly small amounts of by-product is formed in these reactions. A sample of a mixture of (**18a**) and (**18b**) was isolated by preparative scale glc, and the stereochemistries of the per-




Scheme 5.




Scheme 6.

Table 1
Reaction of **6** and **1** with pentafluoropyridine, initiated by CsF[a]

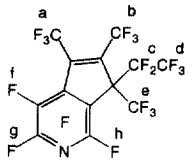
| Monomer | [I]/[M][b] | Temperature (°C) | Time (h) | Volatile products (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | **13** | **14** | **15a** | **15b** | **21** | **16** | **P**[c] |
| **6** | 0.5 | 60 | 24 | 9 | 4 | 2 | 10 | trace | 1 | 0 |
| | 0.5 | 100 | 24 | 1 | 4 | 1 | 5 | 4 | 3 | 0 |
| | 0.5 | 100 | 168 | 2 | 3 | 4 | 12 | 18 | 13 | 0 |
| | 0.02 | 100 | 168 | trace | 9 | 4 | 10 | trace | 5 | 0 |
| | 0.02 | 60 | 168 | 5 | 3 | 3 | 10 | trace | 1 | 0 |
| **1** | 0.5 | 60 | 168 | trace | trace | trace | 1 | trace | 0 | 60 |

[a]Amount of monomers: 18.5 mmol, sulpholan: 20 ml. Molar ratio of pentafluoropyridine to monomer [Py]/[M] = 0.33.
[b]Molar ratio of CsF to monomer.
[c]Poly(hexafluoro-2-butyne).

fluoro-2-butenyl groups were derived by Nmr from coupling constants, where $J_{CF_3-F}$-*trans* is known to be greater than $J_{CF_3-F}$-*cis* [8–12].

For comparison with published data on the polymerization of hexafluoro-1,3-butadiene (**6**), reactions initiated by caesium fluoride in a solvent at 100°C were carried out. It has been possible to compare reactions of **6** and **1** under these conditions and the results are summarized in Table 1.

There are several points to note from these experiments. Under the higher temperature conditions pentafluoropyridine (**12**) is a very effective trap because only small amounts of oligomer (**13**) were observed and no insoluble polymer was obtained. Furthermore, the products were similar to those described above but with one exception, i.e., compound (**21**).



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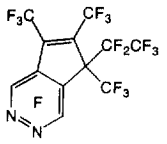

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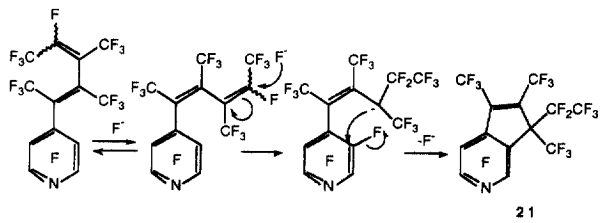
A sample of **21** was separated by preparative scale glc and the structure was established by $^{19}F$ NMR and mass-spectrometry. The $^{19}F$ NMR spectrum showed four different trifluoromethyl groups: three of these occurred at ca. $\delta_F$ −55 to −60 ppm, closely analogous to the $\delta_F$ values for hexakis(trifluoromethyl)cyclopentadiene [13] ($\delta_F$ −55.6, −59.4, and −59.7 ppm), and the other resonance occured at ca. $\delta_F$ −80 ppm, which is characteristic of trifluoromethyl attached to a difluoromethylene group. Furthermore, the system showed three further resonances in the $^{19}F$ NMR spectrum, assigned to fluorine attached to a pyridine ring. These data, coupled with comparison with the data obtained for **22**, observed previously in the reaction of hexafluorobut-2-yne (**1**) with tetrafluoropyridazine [8–12] confirms the structure. The mechanism of formation of **21** is indicated in Scheme 7 and it is very unusual for displacement of fluorine from the 3-position to occur, except in perfluoro-2,4-dialkylpyridine derivatives [14].



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Scheme 7.

The results described in this paper confirm the conclusion derived from studies on the polymerisation of hexafluoro-1,3-butadiene (**6**) with fluoride ion [4]. Thus, we have established that the conversion of **6** to **1**, Scheme 2, occurs faster than reaction of **7** with **6** because no evidence for trapping of intermediate anions derived from **9**, Path B, was observed, even with pentafluoropyridine at high temperature. Therefore, we conclude that polymerisation of **6** occurs by Path A shown in Scheme 2 and in the light of the experiments described above, it is highly unlikely that systems could be found for trapping **9**.

## 3. Experimental

All materials were obtained commercially and used as received except tetrafluoropyrimidine which was made from tetrachloropyrimidine on heating to 480°C in an autoclave with potassium fluoride [15]. Caesium fluoride was dried at 120°C in vacuo overnight before use. All solvents were dried prior to use by standard procedures. $^{19}F$ NMR spectra were recorded using either a Varian VXR 400S or a Bruker AC250 NMR spectrometer. $CFCl_3$ and $Me_4Si$ were used as internal standards and coupling constants are given in Hz. Solid-state $^{19}F$ and $^{13}C$ NMR spectra were recorded on Chemagnetics CMX200 and a Varian Unity Plus spectrometers, respectively. Infrared spectra were measured on a Perkin Elmer 1600 infrared spectrometer. Glc-ms were obtained using a VG Trio 1000 spectrometer linked to a Hewlett-Packard 5890 Series II gas chromatograph fitted with a 25-m cross-linked silicone capillary column. Preparative scale glc was performed on a Shimadsu GC 8A gas chromatograph, equipped with a 3-m 104 silicone elastomer SE30 packed column.

### 3.1. Oligomerization initiated by caesium fluoride

#### 3.1.1. Hexafluoro-1,3-butadiene (6)

A flask was charged with dry caesium fluoride (1.5 g, 10.0 mmol) and sulpholan (20 ml), frozen and evacuated. Hexafluoro-1,3-butadiene (2.7 g, 16.6 mmol) was introduced to the flask via a bladder and the mixture was heated to 100°C. After 24 h, the reaction was cooled in liquid air and the product was isolated by precipitation with methanol and dried to constant weight to give poly(hexafluorobut-2-yne) (1.5 g, 56% conversion based on **6**) as a yellowish white powder; $\upsilon_{max}/cm^{-1}$ 1170, 1200 and 1239 (C–F stretching vibrations of $CF_3$); $\delta_F$ (solid state) −61.3 (broad s, $-C(CF_3)=C(CF_3)$; $\delta_C$ (solid state) 119.9 (broad s, $-C(CF_3)=C(CF_3)-$), 132.8 (broad s, $-C(CF_3)=C(CF_3)-$); as compared to literature data [16].

#### 3.1.2. Hexafluorobut-2-yne (1)

By a similar procedure to that described above, caesium fluoride (4.0 g, 26.5 mmol) and hexafluorobut-2-yne (8.2 g, 50.6 mmol) in sulpholan (40 ml) gave poly(hexafluorobut-2-yne) (7.4 g, 90% conversion based on **1**) as a yellowish white powder; $\upsilon_{max}/cm^{-1}$ 1170, 1200 and 1239 (C–F stretching vibrations of $CF_3$); $\delta_F$ (solid state) −61.2 (broad s, $-C(CF_3)=C(CF_3)-$); $\delta_C$ (solid state) 120.3 (broad s, $-C(CF_3)=C(CF_3)-$), 133.0 (broad s, $-C(CF_3)=C(CF_3)-$); as compared to literature data [16].

### 3.2. Oligomerization initiated by tetrakis(dimethylamino)-ethene (10)

#### 3.2.1. Hexafluoro-1,3-butadiene (6)

A flask was charged with tetrakis(dimethylamino)ethene (0.2 g, 1.0 mmol) under dry nitrogen, frozen and evacuated. Hexafluoro-1,3-butadiene (3.0 g, 18.5 mmol) was introduced into the stirred, cooled (0°C) mixture via a bladder. After 6 h, the reaction was cooled in liquid air and gaseous products (2.5 g, 83% based on **6**) were collected in the gas reservoir at room temperature and identified as a mixture of **6** (97% by NMR); $\delta_F$ −92.9 (2F, m, *cis*-$CF_2$=CF–CF=$CF_2$), −107.4 (2F, m, *trans*-$CF_2$=CF–CF=$CF_2$), −180.0 (2F, m, $CF_2$=$CF$–$CF$=$CF_2$); and **1** (3%); $\delta_F$ −53.7 (s, $CF_3-C\equiv C-CF_3$). Other volatile products were removed from the reaction mixture by distillation under high vacuum (60°C, <1 mm Hg) and identified by $^{19}F$ NMR and GC/MS as a mixture of (i) dimer (43%); *m/e* ($EI^+$) 344 ($M^+$, 0.8%), 325 ($M^+$–F, 50%), 275 ($M^+$–$CF_3$, 75), 225 ($M^+$–$CF_2CF_3$, 23), 187 ($M^+$–F–$(CF_3)_2$, 37), 137 ($M^+$–$(CF_3)_3$, 30), 113 ($CHCFCF_3^+$, 28), 69 ($CF_3^+$, 100), (ii) trimer (42%); *m/e* ($EI^+$) 506 ($M^+$, 1%), 487 ($M^+$–F, 32), 437 ($M^+$–$CF_3$, 21), 387 ($M^+$–$CF_2CF_3$, 28), 349 ($M^+$–F–$(CF_3)_2$, 34), 299 ($M^+$–$(CF_3)_3$, 45), 249 ($M^+$–$CF_2$–$(CF_3)_3$, 22), 119 ($CF_2CF_3^+$, 20), 69 ($CF_3^+$, 100); and (iii) tetramer (15%); *m/e* ($EI^+$) 668 ($M^+$, 0.4%), 649 ($M^+$–F, 2), 599 ($M^+$–$CF_3$, 2), 119 ($CF_2CF_3^+$, 13), 69 ($CF_3^+$, 100). $^{19}F$ NMR of the product mixture showed many peaks; $\delta_F$ ($CDCl_3$) −55 to −65 (F–(–C($CF_3$)=C($CF_3$)–)$_n$–H), −68 to −72 (*F*–(–C($CF_3$)=C($CF_3$)–)$_n$–H); $^1H$ NMR of the product mixture showed $\delta_H$ ($CDCl_3$) 6.72 (q, F–(–C($CF_3$)=C($CF_3$)–)$_2$–*H*) consistent with structures of oligomers.

#### 3.2.2. Hexafluorobut-2-yne (1)

By a similar procedure to that described above, tetrakis-(dimethylamino)ethene (0.2 g, 1.0 mmol) and hexafluorobut-2-yne (3.0 g, 18.5 mmol) gave unreacted monomer (2.4 g, 80%) and oligomers (mixture of dimer (61%), trimer (29%) and tetramer 10%), 0.6 g, 20% based on **1**); GC/MS and $^{19}F$ NMR data as described above.

### 3.3. Trapping reactions with pentafluoropyridine (12)

#### 3.3.1. Hexafluoro-1,3-butadiene (6) initiated by TDAE(10)

A flask was charged with tetrakis(dimethylamino)ethene (0.2 g, 1.0 mmol) and pentafluoropyridine (1.1 g, 6.5 mmol) under dry nitrogen, frozen and evacuated. Hexafluoro-1,3-butadiene (3.0 g, 18.5 mmol) was introduced into the flask via a bladder at room temperature. After 24 h, the reaction was quenched by cooling in liquid air. Volatile products (2.3 g, 55% based on starting materials) were removed by distillation under high vacuum (60°C, <1 mm Hg). Glc-ms analysis showed that this volatile product was a multi component mixture consisting of (i) pentafluoropyridine (**12**) (conversion 75%); *m/e* ($EI^+$) 169 ($M^+$, 100), 150 ($M^+$–F, 22), 138 ($M^+$–CF, 20), 124 ($(CF)_4^+$, 37), 100 ($(C-(CF)_2-N$, 44), 93 ($(CF_2)_3^+$, 27), 69 ($CF_3^+$, 19), 31 ($CF^+$, 32), (ii) oligomers of hexafluoro-1,3-butadiene (**13**, dimer: 7%, trimer: 2%, tetramer: 1%; mass spectral data as shown above, (iii) perfluoro-2-(4-pyridyl)butene (**14**) (7%); *m/e* ($EI^+$) 331 ($M^+$, 71%), 312 ($M^+$–F, 29), 262 ($M^+$–$CF_3$, 100), 212 ($M^+$–$CF_2CF_3$, 31), 193 ($M^+$–$(CF_3)_2$, 17), 69 ($CF_3^+$, 37), (iv) *trans*, *trans*-perfluoro-3,4-dimethyl-2-(4-pyridyl)hexa-2,4-diene (**15a**) (5%); *m/e* ($EI^+$) 493 ($M^+$, 18%), 474 ($M^+$–F, 8), 424 ($M^+$–$CF_3$, 4), 355 ($M^+$–$(CF_3)_2$, 6), 336 ($M^+$–F–$(CF_3)_2$, 9), 286 ($M^+$–$(CF_3)_3$, 15), 69 ($CF_3^+$, 100), (v) *cis*, *trans*-perfluoro-3,4-dimethyl-2-(4-pyridyl)hexa-2,4-diene (**15b**) (37%); *m/e* ($EI^+$) 493 ($M^+$, 27%), 474 ($M^+$–F, 16), 424 ($M^+$–$CF_3$, 8), 355 ($M^+$–$(CF_3)_2$, 11), 336 ($M^+$–F–$(CF_3)_2$, 18), 286 ($M^+$–$(CF_3)_3$, 33), 69 ($CF_3^+$, 100), and, (vi) perfluoro-3,4,5,6-tetramethyl-2-(4-pyridyl)octa-2,4,6-triene (**16**) (12%); *m/e* ($EI^+$) 655 ($M^+$, 6%), 448 ($M^+$–$(CF_3)_3$, 3), 379 ($M^+$–$(CF_3)_4$, 3), 360 ($M^+$–F–$(CF_3)_4$, 4), 310 ($M^+$–$(CF_3)_5$, 5), 293 ($M^+$–$C_8F_{14}$, 7), 200 ($C_4F_8$, 9), 119 ($CF_2CF_3^+$, 8), 69 ($CF_3^+$, 100). The composition of the mixture was estimated by GC integration and yields were calculated based on conversion of starting materials. Using preparative scale glc, component (v) was separated and identified as *cis*, *trans*-perfluoro-3,4-dimethyl-2-(4-pyridyl)hexa-2,4-diene (**15b**); $\delta_F$ ($CDCl_3$) −59.9 (3F, d, $J_{1-CF_3,3-F}$ 15, 1-$CF_3$), −61.6 (6F, m, 3- and 4-$CF_3$), −69.3 (3F, m, 5-$CF_3$), −86.7 (2F, m, 2- and 6-F of pyridine),

−103.6 (1F, q, $J_{5-F,4-CF_3}$ 8, 5-F), −138.5 (2F, m, 3- and 5-F of pyridine); as compared to literature data [3]. This component also contained a trace amount of *trans*-isomer, **15a**.

### 3.3.2. Hexafluoro-1,3-butadiene (6) initiated by caesium fluoride in sulpholan

A flask charged with dry caesium fluoride (1.5 g, 10.0 mmol), pentafluoropyridine (1.6 g, 9.5 mmol) and sulpholan (20 ml) was frozen and evacuated. Hexafluoro-1,3-butadiene (4.5 g, 27.6 mmol) was introduced into the flask via a bladder and the reaction mixture was heated at 100°C. After 168 h, the reaction was quenched by cooling in liquid air. Volatile products (3.5 g, 57% based on starting materials) were collected by distillation under high vacuum (60°C, < 1 mm Hg). Glc-ms analysis showed that this volatile product was a multi component mixture. Components (iii), (v), (vi) and (vii) were separated and analysed by $^{19}F$ NMR spectroscopy, assignments of $^{19}F$ NMR were based on the literature values [3]. Glc-ms gave (i) pentafluoropyridine (**12**) (conversion 57%); (ii) dimer of hexafluoro-1,3-butadiene (**13**, $n=2$) (2%); (iii) perfluoro-2-(4-pyridyl)butene (**14**) (3%); $\delta_F$ ($CDCl_3$) −63.6 (3F, s, 2-$CF_3$), −71.0 (3F, s, 1-$CF_3$), −87.0 (2F, m, 2- and 6-F of pyridine), −109.0 (1F, q, $J_{5-F,4-CF_3}$ 8.0, 1-F), −139.0 (2F, m, 3- and 5-F of pyridine); this component contained trace amounts of *cis*-isomer; (iv) *trans*, *trans*-perfluoro-3,4-dimethyl-2-(4-pyridyl)-hexa-2,4-diene (**15a**) (4%); (v) *cis*, *trans*-perfluoro-3,4-dimethyl-2-(4-pyridyl)hexa-2,4-diene (**15b**) (12%); (vi) perfluoro-3-ethyl-1,2,3-trimethyl-cyclopente[c]pyridine (**21**) (18%); $\delta_F$ ($CDCl_3$) −54.3 (3F, s, b as indicated on the diagram in the text), −60.1 (3F, m, a), −60.9 (3F, m, e), −61.8 (1F, m, h), −76.2 (1F, m, g), −79.9 (3F, s, d), −107.6 (2F, m, c), −139.3 (1F, m, f); *m/e* ($EI^+$) 493 ($M^+$, 21%), 474 ($M^+$–F, 14), 374 ($M^+$–$CF_2CF_3$, 100), 355 ($M^+$–$(CF_3)_2$, 32), 324 ($M^+$–CF–$(CF_3)_2$, 39), 305 ($M^+$–$CF_2$–$(CF_3)_2$, 56), 286 ($M^+$–$(CF_3)_3$, 57), 255 ($M^+$–CF–$(CF_3)_2$, 27), 119 ($CF_2CF_3^+$, 21), 69 ($CF_3^+$, 97); (vii) perfluoro-3,4,5,6-tetramethyl-2-(4-pyridyl)octa-2,4,6-triene (**16**) (13%); *m/e* ($EI^+$) 655 ($M^+$, 6%), 448 ($M^+$–$(CF_3)_3$, 3), 379 ($M^+$–$(CF_3)_4$, 2), 360 ($M^+$–F–$(CF_3)_4$, 4), 310 ($M^+$–$(CF_3)_5$, 5), 293 ($M^+$–$C_8F_{14}$, 7.3%), 200 ($C_4F_8$, 9), 119 ($CF_2CF_3^+$, 8), 69 ($CF_3^+$, 100); $\delta_F$ ($CDCl_3$) −59.9 (3F, s, 2-$CF_3$), −62.1 (12F, s, 3,4,5,6-$CF_3$), −69.9 (3F, 8-$CF_3$), −87.3 (2F, m, 2- and 6-F of pyridine), −104.2 (1F, m, 7-F), −139.0 (2F, m, 3- and 5-F of pyridine).

By a similar procedure to that described above, reaction of hexafluoro-1,3-butadiene with pentafluoropyridine initiated by caesium fluoride in sulpholane gave a product mixture similar to that obtained at 100°C for 168 h. The results are summarized in Table 1.

### 3.3.3. Hexafluorobut-2-yne (1) initiated by TDAE (10)

By a similar procedure to that described above, TDAE (0.4 g, 2.0 mmol), pentafluoropyridine (2.0 g, 11.8 mmol) and hexafluorobut-2-yne (5.0 g, 30.9 mmol) gave similar volatile products (2.3 g, 55% based on starting materials). Glc-ms shows that this volatile product was a multi component mixture consisting of (i) pentafluoropyridine (**12**) (conversion 62%); (ii) oligomers of hexafluorobut-2-yne (**13**, dimer: 2%, trimer: 1%); (iii) perfluoro-2-(4-pyridyl)butene (**14**) (2%); (iv) *trans*, *trans*-perfluoro-3,4-dimethyl-2-(4-pyridyl)hexa-2,4-diene (**15a**) (2%); (v) *cis*, *trans*-perfluoro-3,4-dimethyl-2-(4-pyridyl)hexa-2,4-diene (**15b**) (9%) and (vi) perfluoro-3,4,5,6-tetramethyl-2-(4-pyridyl)octa-2,4,6-triene (**16**) (5%). Poly(hexafluorobut-2-yne) (2.1 g, 31% based on starting materials) was isolated from the reaction residue by precipitation with methanol.

### 3.3.4. Hexafluorobut-2-yne (1) initiated by caesium fluoride in sulpholan

The same procedure for the reaction of hexafluoro-1,3-butadiene described in the former section was used. The products were a mixture of similar compounds to those obtained in reaction of hexafluoro-1,3-butadiene and the result is summarized in Table 1.

### 3.4. Trapping reactions with tetrafluoropyrimidine (17)

### 3.4.1. Hexafluoro-1,3-butadiene (6) initiated by TDAE (10)

A flask charged with TDAE (0.26 g, 1.3 mmol) and pentafluoropyrimidine (1.2 g, 8.6 mmol) under dry nitrogen was frozen and evacuated. Hexafluoro-1,3-butadiene (3.5 g, 21.6 mmol) was introduced into the flask via a bladder at room temperature. After 24 h, the reaction was quenched by cooling in liquid air and volatile products (1.8 g, 38% based on starting materials) were removed by distillation under high vacuum (60°C, < 1 mm Hg). The composition of the mixture was estimated by GC integration and calculated based on conversion of starting materials. Using preparative scale glc, a mixture of (ii) and (iii) and component (iv) were separated and compared to literature data [3]. Glc-ms analysis showed that this volatile product was a multi component mixture consisting of (i) tetrafluoropyrimidine (**17**) (conversion 22%); *m/e* ($EI^+$) 152 ($M^+$, 100%), 133 ($M^+$–F, 12), 107 ($N(CF)_3$, 24), 62 ($(CF)_2^+$, 26), 31 ($CF^+$, 67); (ii) *trans*-perfluoro-4-(1-methyl-4-propenyl)pyrimidine (**18a**) (10%); $\delta_F$ ($CDCl_3$) −48.2 (1F, m, 2-F of pyrimidine), −62.8 (3F, m, 1-$CF_3$), −72.3 (3F, m, 4-$CF_3$), −74.0 (1F, m, 6-F of pyrimidine), −109.4 (1F, m, 3-F), −154.5 (2F, s, 5-F of pyrimidine); this component contained a trace amount of *cis*-isomer; *m/e* ($EI^+$) 314 ($M^+$, 43%), 295 ($M^+$–F, 33), 245 ($M^+$–$CF_3$, 100), 69 ($CF_3^+$, 60), 62 ($(CF)_2^+$, 11), 31 ($CF^+$, 10); (iii) *cis*-perfluoro-4-(1-methyl-4-propenyl)pyrimidine (**18b**) (1%); $\delta_F$ ($CDCl_3$) −48.2 (1F, m, 2-F of pyrimidine), −59.3 (3F, m, 1-$CF_3$), −70.8 (3F, m, 4-$CF_3$), −74.0 (1F, m, 6-F of pyrimidine), −105.6 (1F, m, 3-F), −154.4 (2F, s, 5-F of pyrimidine); *m/e* ($EI^+$) 314 ($M^+$, 43%), 295 ($M^+$–F, 33), 245 ($M^+$–$CF_3$, 100), 69 ($CF_3^+$, 60), 62 ($(CF)_2^+$, 11), 31 ($CF^+$, 10); (iv) perfluoro-4,6-bis(*trans*-2-butenyl)pyrimidine (**19**) (19%); $\delta_F$ ($CDCl_3$) −45.8 (1F, m, 2-F of pyrimidine),

−59.7 (3F, m, 1-$CF_3$), −69.7 (3F, m, 4-$CF_3$), −106.0 (2F, m, 3-F), −132.9 (2F, s, 5-F of pyrimidine); *m/e* ($EI^+$) 476 ($M^+$, 28%), 457 ($M^+$–F, 41), 407 ($M^+$–$CF_3$, 77), 250 ($C_7F_8N^+$, 30), 200 ($C_6F_6N^+$, 67), 155 ($C_5F_5^+$, 37), 69 ($CF_3^+$, 100); (v) 1:3 adduct of tetrafluoropyrimidine and hexafluoro-1,3-butadiene (**20**) (1%).

*3.4.2. Hexafluorobut-2-yne (1) initiated by TDAE (10)*

By a similar procedure to that described above, TDAE (0.27 g, 1.3 mmol), tetrafluoropyrimidine (1.26 g, 8.3 mmol) and hexafluoro-2-butyne (3.6 g, 22.2 mmol) gave liquid products (1.7 g, 35%). Glc-ms shows that this volatile product was a multi component mixture consisting of (i) tetrafluoropyrimidine (**17**) (conversion 24%); (ii) *trans*-perfluoro-4-(1-methyl-4-propenyl)pyrimidine (**18a**) (3%); (iii) *cis*-perfluoro-4-(1-methyl-4-propenyl)-pyrimidine (**18b**) (3%); (iv) perfluoro-4,6-bis(*trans*-2-butenyl)pyrimidine (**19**) (11%); (v) 1:3 adduct of tetrafluoropyrimidine and hexafluorobut-2-yne (**20**) (2%).

## 4. Note added to Proof

Dr. B.E. Smart informs us of similar conclusions from his laboratory concerning the identity of the polymer obtained from fluoride ion induced polymerisation of hexafluoro-1,3-butadiene [see, W. Mahler, B.E. Smart, D.B. Clase, C.M. Foris and R.C. Wheland, Makromol. Chem., Rapid Commun., 13 (1992) 159].

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