

Pyrolysis reactions of nonafluorobiphenyl-4-yl prop-2-enyl ether: a remarkable rearrangement reaction of an intramolecular Diels–Alder product

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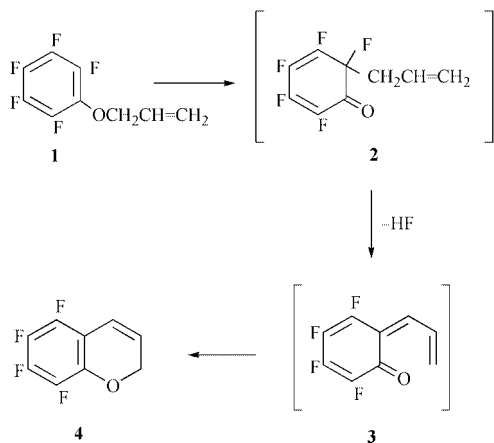
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The title compound **16** on flash vapour pyrolysis (FVP) at 350 °C gives a complex mixture which includes **20**, the product of one of the two possible intramolecular Diels–Alder reactions of the cyclohexa-2,4-dienone intermediate **17** formed *via* a Claisen rearrangement reaction. FVP of **16** at 420 °C gives the bicyclic compound **30**, formed *not* from the other possible Diels–Alder adduct **27** but from an isomer **31** having exactly the same carbon skeleton, but produced as a transient intermediate *via* a rare retro-cyclisation reaction of **20** to a tethered ketene **32** and recyclicalisation *via* the alternative mode.

In an earlier paper,¹ a novel route to 5,6,7,8-tetrafluoro-2*H*-chromene **4** was conceived whereby under flash vapour-phase conditions at low pressure through a silica tube packed with silica wool, pentafluorophenyl prop-2-enyl ether **1** would undergo the Claisen rearrangement to the intermediate **2** which would be followed first by the elimination of hydrogen fluoride and then electrocyclicisation of the *o*-quinomethane-type material **3** (Scheme 1).



Scheme 1

At 365 °C and 0.05 mmHg the cyclohexa-2,5-dienone **5** was formed *via* **2** followed by a Cope rearrangement,² (Scheme 2). Under more vigorous conditions at 440–480 °C, compound **1** gave the 1-fluorovinyl ketone **8** the formation of which was proposed to occur from **2** *via* the decomposition of the intramolecular Diels–Alder adduct **6** to **7** followed by loss of HF³ (Scheme 3). The intermediacy of the *alternative* intramolecular Diels–Alder adduct **9** was proposed to explain the formation of another isomer, the bicyclic compound **11**, *via* the ring-opened species **10**¹ containing two conjugated radicals (Scheme 4). The original objective of synthesising the heterocyclic compound **4** in Scheme 1 was realised eventually by heating **1** in refluxing DMF with potassium fluoride as a base to effect the required dehydrofluorination reaction of the intermediate **2**.⁴

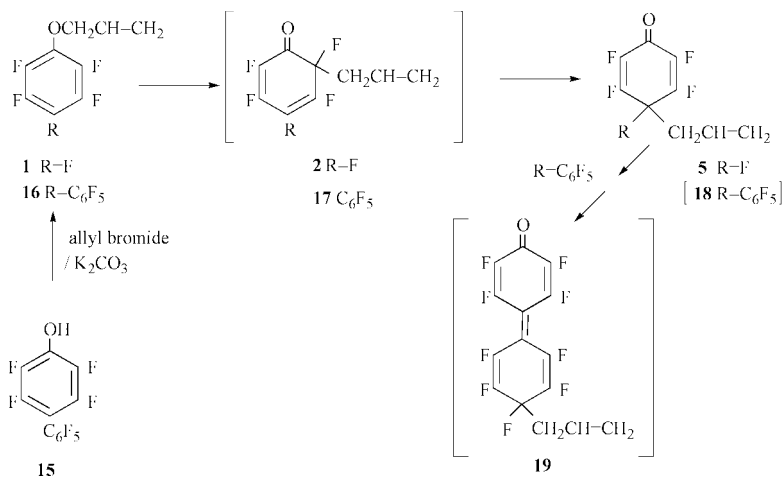
In order to increase significantly the time of reaction, the ether **1** was heated *in vacuo* at 137–141 °C over 13 days and gave two products: the intramolecular Diels–Alder adduct **6**⁵

(invoked in the formation of **8**) and its skeletally related isomer **13** containing a plane of symmetry, isolated as its 1,1-diol hemihydrate **14**.⁶ The formation of **13** was rationalised by invoking an overall [1,3]sigmatropic shift occurring in a step-wise manner from **6**; the species **12** containing two conjugated radicals was proposed as an intermediate (Scheme 3).

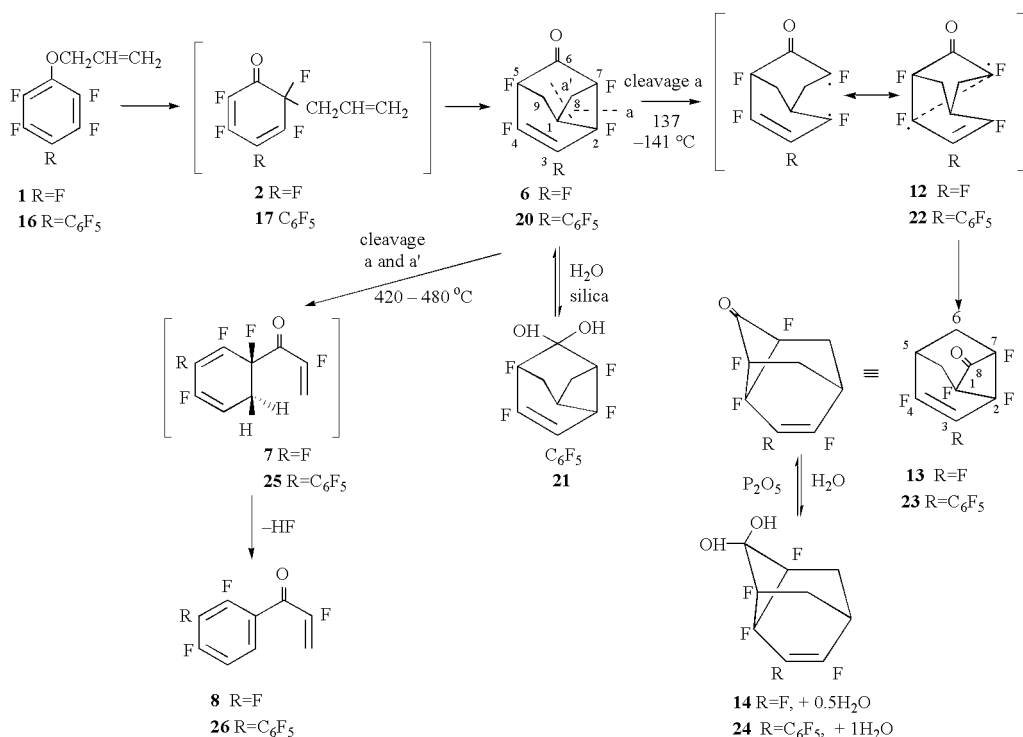
The purpose of the present work was to investigate the pyrolysis reactions of the 4-pentafluorophenyl derivative of **1**, namely compound **16**, and in particular, the possibility of inducing not only the Claisen and Cope rearrangements *via* **17** to **18**, but also two further Cope rearrangement reactions to **19** (Scheme 2), the first of which would involve an aromatic ring in the [3,3]sigmatropic reaction. This latter type of reaction has been studied in another system, but no rearrangement occurred.⁷ In the present work, *no* isomerisations of **16** to **18** or **19** were detected: some chemistry analogous to our earlier work was found, but another truly remarkable rearrangement reaction was discovered which has been reported in a preliminary communication.⁸

Results and discussion

The starting material **16** was prepared from the known nonafluoro-4-hydroxybiphenyl **15**⁹ and prop-2-enyl bromide (Scheme 2) and was subjected to FVP at 350 °C and 0.01 mmHg as before to give a complex mixture of products, clearly evidenced from the ¹⁹F NMR spectrum. The major component (67%) of the products was unreacted **16** (Scheme 3) which was efficiently removed in the supernatant liquid from solid materials which had crystallised from light petroleum at –18 °C. Chromatography of the solid enabled the Diels–Alder adduct **20** to be isolated, the structure of which was determined by X-ray crystallography.⁸ The ¹⁹F NMR spectra of the fractions from the chromatography immediately following **20** showed the presence of another closely related compound having three of the resonances at low frequencies shifted to even lower frequencies by *ca.* 1.3–4.5 ppm. In a separate experiment, chromatography of **20** on silica resulted in its being converted to this new species **21**, contaminated with 15% of **20**, and it was assigned the *gem*-diol structure (the result of facile hydration due to adventitious water on the stationary phase during separation) on the basis of the strong O–H absorptions in the IR spectrum. The next material isolated by chromatography was a mixture of closely related compounds **23** and **24** which on



Scheme 2



Scheme 3

crystallisation from water gave the stable *gem*-diol monohydrate **24** and which in turn could be dehydrated with P₂O₅ to the ketone **23** contaminated with 4% **24**. The structures of **23** and **24** were determined by ¹⁹F NMR spectroscopy which showed the presence of a plane of symmetry in the molecules because the intensities of the absorptions at -186.4 and -194.6 ppm respectively were twice those at -201.4 and -202.2 ppm (the bridgehead fluorines), and by analogy of these shifts with those in **14** whose structure had been determined by X-ray crystallography (the details of which were not reported),⁶ and which has since been repeated (Fig. 1).¹⁰

When the pyrolysis of **16** was carried out at 420 °C and 0.01 mmHg as before, the ¹⁹F NMR spectrum of the crude product showed the presence of three major components, one of which was identified by the presence of a unique absorption at *ca.* -140 ppm as the phenol **15** (presumably formed by homolytic cleavage of the O-CH₂ bond in the ether followed by a hydrogen atom abstraction reaction), as well as very small proportions of **20**, **21**, **23** and **24**. Chromatography of the material gave a liquid readily identified as the 1-fluorovinyl ketone **26** by ¹⁹F and ¹H NMR spectroscopy and by analogy with data found for compound **8** studied earlier³ (Scheme 3). The pyrolysis reac-

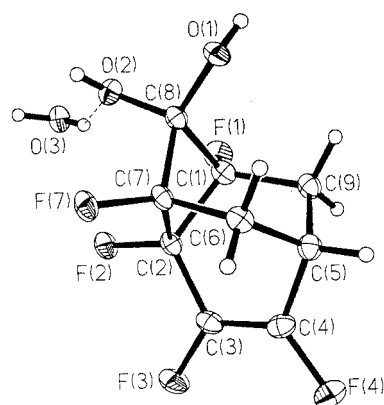
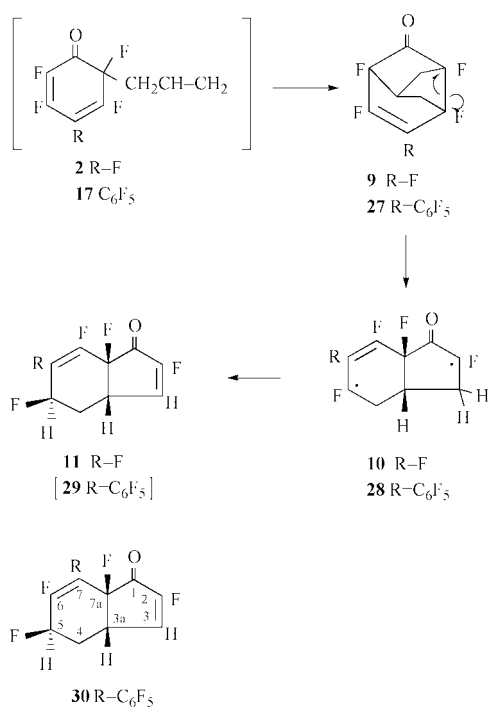


Fig. 1 X-Ray crystal structure of **14**· $\frac{1}{2}$ H₂O.

tion was repeated under identical conditions and the crude product was crystallised from light petroleum at -18 °C to give a solid which had all the superficial ¹⁹F and ¹H NMR spectral properties (principally chemical shifts and a *gem*-CHF group *J*_{5aH-5bF} 49.3 Hz) expected of compound **29**,



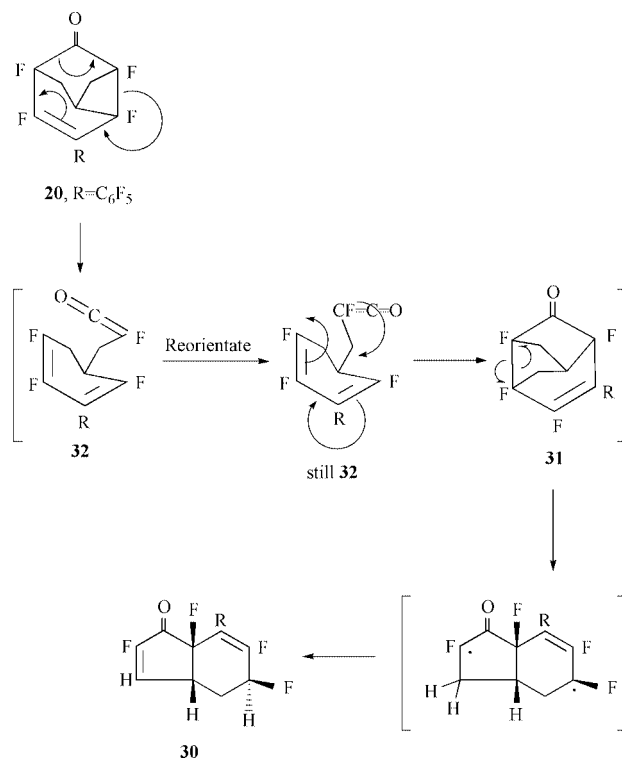
Scheme 4

analogous to **11** (Scheme 4). However, the ^{19}F COSY data indicated some unusual values for $J_{\text{F-F}}$ for structure **29**. The structure of the bicyclic compound **11** had been assigned on the basis of further chemical evidence,¹ but an X-ray crystallographic analysis was carried out on the suspected bicyclic compound which, surprisingly, showed it to be the isomer **30** (Scheme 4); this structure immediately rationalised the NMR data and also showed that the Diels–Alder adduct **27** cannot have been formed from **17** during the reaction and therefore a new mechanism has to be proposed. At 350 °C, new products identified by ^{19}F NMR were present in the crude product to the extent of 39%: **15**, **20**, **21**, **23**, **24**, **26** and **30** being present in the ratio 19:28.5:0.5:35:4.5: 4.5:7; at 420 °C, 70% of the following identifiable compounds were present in the crude product: **15**, **16**, **20**, **21**, **23**, **24**, **26** and **30** being present in the ratio 41:8:1:0.5:1:0.5:22:26. All five fluorines in the C_6F_5 groups in compounds **20**, **21** and **30** were observed, which is indicative of restricted rotation.

In the earlier work, the formation of **11** was readily explained as arising from the *alternative* Diels–Alder adduct **9** via homolytic cleavage of a C–C bond to give the diradical **10**, the flexibility of which allowed the close approach of the radical in the six-membered ring to abstract hydrogen from the CH_2 group in the five-membered ring. It was also pointed out that simple molecular models indicate that the formation of adducts of the type **6** (and therefore **20**) should be much easier than those of type **9** (and therefore **27**).¹ Nevertheless, an intermediate **31** having the same basic carbon skeleton as **27** but having the alkenic F and R groups interchanged, is required as the precursor to **30** and we propose its formation from **20** via a retro-Diels–Alder reaction to give the cyclohexa-2,4-dienylmethyl fluoroketene **32**, a rare reaction type,¹¹ followed by the *alternative* Diels–Alder cyclisation as shown in Scheme 5; compound **30** is racemic, but has the enantiomeric structure shown when formed in this way from **20**.

Intermolecular (4+2) π reactions of ketenes to form six-membered *carbocyclic* rings (as opposed to oxygen-containing rings by involvement of the C=O bond) are uncommon.¹² However, there is one recorded example of an intramolecular process of this type in the literature.¹³

The conclusion to be drawn from these experiments has to be that while the formation of internal Diels–Alder adducts having



Scheme 5

the structures **6** and **20** does take place (the former type occurring even under relatively mild conditions⁵) and the formation of the alternative one **27** does not arise from the 2,4-dienone **17** for steric reasons, the *alternative circuitous route* to **31** starting from **20** is favourable nevertheless, though it is not obvious why this should be so; even the formation of **11** is likely to proceed *via* this new molecular rearrangement reaction. Further substituted materials analogous to **16** are currently being investigated to assess the generality of the rearrangement.

Experimental

NMR spectra were recorded on the following instruments at the frequencies listed: Varian Mercury 200 (^1H , 199.991 MHz; ^{19}F , 188.179 MHz) and Varian VXR 400 (^1H , 399.952 MHz; ^{19}F , 376.346 MHz). Chemical shifts are reported using the high-frequency positive convention from TMS and CFCl_3 , hence ^{19}F resonance values are negative; J values are in Hz; ^{19}F COSY experiments were carried out on compounds **16**, **20**, **26** and **30** to establish connectivities. Elemental analyses were performed on an Exeter Analytical Inc CE440 elemental analyser.

Nonafluoro-4-hydroxybiphenyl 15

Compound **15** was prepared in 68% yield from decafluorobiphenyl by the method given in the literature⁹ (41%); $\delta_{\text{F}}(\text{CDCl}_3)$ -137.6 (m, 2'-F, 6'-F), -139.4 (m, 3-F, 5-F), -150.8 (tt, 4'-F), -160.7 (tm, 3'-F, 5'-F), -162.0 (dm, 2-F, 6-F).

Nonafluorobiphenyl-4-yl prop-2-enyl ether 16

A mixture of nonafluoro-4-hydroxybiphenyl **15** (14.91 g), allyl bromide (15 ml) and potassium carbonate (20.0 g) in acetone (150 ml) was heated under reflux for 16 h, filtered, the solvent removed *in vacuo* at 30 °C and the residue distilled to give nonafluorobiphenyl-4-yl prop-2-enyl ether **16** (16.44 g, 98%); bp 82 °C at 0.02 mmHg (Found: C, 48.22; H, 1.30. $\text{C}_{15}\text{H}_5\text{F}_9\text{O}$ requires C, 48.41; H, 1.35%); $\delta_{\text{F}}(\text{CDCl}_3)$ -137.5 (m, 2'-F, 6'-F), -139.6 (m, 3-F, 5-F), -150.8 (tt, 4'-F), -155.4 (dm, 2-F, 6-F), -160.8 (tm, 3'-F, 5'-F); $\delta_{\text{H}}(\text{CDCl}_3)$ 4.84 (d, CH_2H_a), 5.36 (d,

H_d), 5.46 (d, H_c), 6.07 (m, H_b) in $-\text{CH}_a\text{H}_b\text{CH}_c=\text{CH}_d$ where H_b and H_d are *Z*-configuration.

Pyrolysis of nonafluorobiphenyl-4-yl prop-2-enyl ether **16**

(a) At 350 °C. The ether **16** (2.45 g) was distilled *in vacuo*, in five consecutive experiments using *ca.* 0.5 g per experiment, from a silica boat through a silica tube (510 × 20 mm) packed in the middle 170 mm with silica wool. The packing only in the tube was heated to 350 °C with the boat initially at one end of the closed tube at room temperature, the other end being connected to a high vacuum system *via* a trap cooled in liquid air. When the pressure had reached 0.01 mmHg, the pyrolysis tube was moved to allow the boat and contents to enter the hot zone of the heating oven and a hot air gun was used to vaporise any condensate beyond the exit of the oven into the trap. Each experiment took approximately 15 minutes and each pyrolysate was washed from the trap with ether. The solvent was distilled from the combined solutions and a ¹⁹F NMR was run of a sample in CDCl₃ to allow, ultimately, an analysis of the complex composition (see later). The crude reaction product was dissolved in light petroleum (bp 40–60 °C) and left for 15 h in a freezer at –18 °C. A solid (0.81 g) was separated by decanting it from the supernatant solution which contained a high proportion of unreacted starting material **16** and was not examined further. The solid was chromatographed on silica using diethyl ether as eluant to give four compounds: (i) 3-pentafluorophenyl-2,4,5,7-tetrafluorotricyclo[3.3.1.0^{2,7}]non-3-en-6-one **20**, mp 140–141 °C (from light petroleum bp 80–100 °C) (Found: C, 48.22; H, 1.35. C₁₅H₅F₉O requires C, 48.41; H, 1.35%); δ_F(CDCl₃) –116.1 (s, 4-F), –136.4 (br s, 2'-F), –138.1 (br d, 6'-F), –150.6 (t, 4'-F), –160.2 (td, 3'-F), –160.8 (td, 5'-F), –175.0 (m, 7-F), –193.0 (m, 5-F), –198.1 (d, 2-F); δ_H(CDCl₃) 2.16 (d, 1-H), 2.34 (m, one H), 2.42 (m, one H), 3.10 (m, one H), 3.24 (m, one H); ν_{max} 1775 cm⁻¹ (C=O). (ii) the next fractions contained mixtures of **20** and a closely related compound (from the ¹⁹F NMR spectra) which in separate chromatography on silica provided an enriched mixture containing **20** (15 parts) and 3-pentafluorophenyl-2,4,5,7-tetrafluorotricyclo[3.3.1.0^{2,7}]non-3-ene-6,6-diol **21** (85 parts), δ_F(CDCl₃) –114.6 (s, 4-F), –137.2 (br s, 2'-F), –138.5 (br d, 6'-F), –152.5 (t, 4'-F), –161.4 (td, 3'-F), –161.7 (td, 5'-F), –178.0 (m, 7-F), –197.4 (m, 5-F), –199.3 (d, 2-F); ν_{max} 3566 and 3427 cm⁻¹ (O–H). (iii) the third and fourth components were a mixture of a ketone and its related 1,1-diol: recrystallisation from water gave 3-pentafluorophenyl-1,2,4,7-tetrafluorotricyclo[3.3.1.0^{2,7}]non-3-ene-8,8-diol monohydrate **24**, mp 98–99 °C (Found: C, 44.46; H, 1.96. C₁₅H₇F₉O₂·1H₂O requires C, 44.13; H, 2.22%); δ_F(CDCl₃) –98.6 (s, 4-F), –138.1 (m, 2'-F, 6'-F), –152.6 (t, 4'-F), –161.7 (td, 3'-F, 5'-F), –194.6 (d, 1-F, 7-F), –202.2 (m, 2-F); δ_H(CDCl₃) 1.59 (s, H₂O), 1.79 (m, two H), 2.72 (m, two H), 2.95 (m, two OH), 3.92 (d, 5-H); ν_{max} 3548 cm⁻¹ (*gem*-diol); sublimation from a mixture of **24** and four times its weight of P₂O₅ *in vacuo* at 55 °C/0.01 mmHg gave an enriched mixture containing **24** (4 parts) and 3-pentafluorophenyl-1,2,4,7-tetrafluorotricyclo[3.3.1.0^{2,7}]non-3-en-8-one **23** (96 parts); δ_F(CDCl₃) –98.1 (s, 4-F), –137.9 (m, 2'-F, 6'-F), –151.4 (t, 4'-F), –161.0 (td, 3'-F, 5'-F), –186.4 (d, 1-F, 7-F), –201.4 (m, 2-F); δ_H(CDCl₃) 2.18 (td, two H), 2.68 (d, two H), 3.13 (d, 5-H); ν_{max} 1831 (C=O), 1697 cm⁻¹ (CF=CC₆F₅).

(b) At 420 °C. The ether **16** (2.349 g) was pyrolysed in five batches of *ca.* 0.5 g at 420 °C as described in (a) and again the ¹⁹F NMR was run in CDCl₃ to allow, ultimately, an analysis of the complex composition (see later). The crude reaction product was dissolved in light petroleum (bp 40–60 °C) and

left for 15 h in a freezer at –18 °C, and the solid (0.271 g) which separated was recrystallised from light petroleum (bp 80–100 °C) to give 7-pentafluorophenyl-2,5β,6,7αβ-tetrafluoro-3αβ,4,5,7a-tetrahydro-1H-inden-1-one **30**, mp 135–136 °C (Found: C, 48.35; H, 1.25. C₁₅H₅F₉O requires C, 48.41; H, 1.35%); δ_F(CDCl₃) –99.2 (d, 6-F), –132.9 (d, 2-F), –137.3 (tt, 2'-F), –137.8 (d, 6'-F), –151.0 (tt, 4'-F), –154.5 (t, 7αβ-F), –160.9 (td, 3'-F), –161.3 (td, 5'-F), –194.4 (dm, 5β-F); δ_H(CDCl₃) 2.48 (m, two 4-H), 3.59 (dm, 4α-H), 5.16 (dm, 5α-H, J_{5αH-5βF} 49.3), 6.94 (t, 3-H); ν_{max} 3083 (C–H), 1747 (C=O), 1701 (CF=CC₆F₅), 1651 cm⁻¹ (CF=CH).

In a separate experiment, the crude product from the pyrolysis of the ether **16** (1.965 g) was chromatographed on silica using light petroleum (bp 40–60 °C)–diethyl ether (95:5% v/v) to give 1-fluorovinyl 3-pentafluorophenyl-2,4-difluorophenyl ketone **26** (0.309 g), a liquid which rapidly polymerises in air (Found: C, 51.23; H, 1.18. C₁₅H₄F₈O requires C, 51.16; H, 1.14%); δ_F(CDCl₃) –102.0 (m, 4-F), –107.3 (m, 2-F), –114.9 (m, F_a), –137.5 (m, 2'-F, 6'-F), –151.1 (tt, 4'-F), –161.0 (tm, 3'-F, 5'-F); δ_H(CDCl₃) 5.40 (s, H_a), 5.54 (dd, H_b, J_{Fa-Hb} 32, J_{Ha-Hb} 2 in C_{Fa}=CH_aH_b where F_a and H_b are *E*), 7.10 (t), 7.68 (q) are unassigned H₅, H₆; ν_{max} 1691 cm⁻¹ (C=O).

Product ratios from the pyrolysis reactions

(a) At 350 °C. In the ¹⁹F NMR spectrum of the crude product, the integrations equivalent to one fluorine of a *unique* absorption in every identifiable component in the mixture were related to the integrations of *all* the 4'-F's (all triplets) in C₆F₅ groups between –150.7 and –152.8 ppm (which provided a measure of *all* the molecular species present) and gave the total proportion of these components in the mixture as 39%, compounds **15**, **20**, **21**, **23**, **24**, **26** and **30** being present in the ratio 19:28.5:0.5:35:4.5:4.5:7.

(b) At 420 °C. 70% of the following identifiable compounds were present in the crude product: **15**, **16**, **20**, **21**, **23**, **24**, **26** and **30** being present in the ratio 41:8:1:0.5:1:0.5:22:26.

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- 10 Crystal data: C₉H₇F₅O₂·½H₂O, *M* = 251.15, *T* = 120 K, monoclinic, space group *C2/c* (no. 15) *a* = 25.133(7), *b* = 6.757(2), *c* = 11.032(4) Å, β = 105.44(2)°, *U* = 1806(1) Å³, *Z* = 8 (H₂O on axis 2), *D*_{calc} = 1.85 g cm⁻³, SMART CCD area detector, Mo-Kα radiation, SHELXL97 software, 6231 reflections (2θ ≤ 55°), 2064 unique, *R* = 0.034 [1703 data with *F*² ≥ 2σ(*F*²)], *wR*(*F*²) = 0.088. Full data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre. CCDC reference number 207/419. See <http://www.rsc.org/suppdata/p1/b0/b001356k/> crystallographic files in .cif format.
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