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

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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 recyclisation *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 electrocyclisation of the *o*-quinomethane-type material **3** (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 stepwise 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 15⁹ 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

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crystallisation from water gave the stable *gem*-diol monohydrate 24 and which in turn could be dehydrated with P_2O_5 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 $14 \cdot \frac{1}{2}$ 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 $J_{5aH-5\beta F}$ 49.3 Hz) expected of compound **29**,



Scheme 4

analogous to 11 (Scheme 4). However, the ¹⁹F 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 ¹⁹F 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 CH₂ 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 sixmembered *carbocyclic* rings (as opposed to oxygen-containing rings by involvment 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



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; ¹⁹F, 188.179 MHz) and Varian VXR 400 (¹H, 399.952 MHz; ¹⁹F, 376.346 MHz). Chemical shifts are reported using the high-frequency positive convention from TMS and CFCl₃, hence ¹⁹F resonance values are negative; *J* values are in Hz; ¹⁹F 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%); $\delta_{\rm F}({\rm CDCl}_3)$ -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. C₁₅H₅F₉O requires C, 48.41; H, 1.35%); $\delta_{\rm F}$ (CDCl₃) –137.5 (m, 2'-F, 6'-F), –139.6 (m, 3'-F, 5'-F); $\delta_{\rm H}$ (CDCl₃) 4.84 (d, CH_aH_a), 5.36 (d,

 H_d), 5.46 (d, H_c), 6.07 (m, H_b) in $-CH_aH_aCH_b=CH_cH_d$ 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 $(510 \times 20 \text{ mm})$ 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); $\delta_{\rm H}$ (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); v_{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-3ene-6,6-diol 21 (85 parts), $\delta_{\rm F}({\rm CDCl_3})$ -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); v_{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-8,8diol monohydrate 24, mp 98-99 °C (Found: C, 44.46; H, 1.96. $C_{15}H_7F_9O_2 \cdot 1H_2O$ requires C, 44.13; H, 2.22%); $\delta_F(CDCl_3)$ -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); $\delta_{\rm H}$ (CDCl₃) 1.59 (s, H_2 O), 1.79 (m, two H), 2.72 (m, two H), 2.95 (m, two OH), 3.92 (d, 5-H); v_{max} 3548 cm⁻¹ (gem-diol); sublimation from a mixture of 24 and four times its weight of P_2O_5 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); $\delta_{\rm F}({\rm CDCl}_3)$ -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); $\delta_{\rm H}({\rm CDCl_3})$ 2.18 (td, two H), 2.68 (d, two H), 3.13 (d, 5- H); v_{max} 1831 (C=O), $1697 \text{ cm}^{-1} (\text{CF}=\text{CC}_6\text{F}_5).$

(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,6,7aβ-tetrafluoro-3aβ,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%); $\delta_{\rm F}$ (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, 7aβ-F), -160.9 (td, 3'-F), -161.3 (td, 5'-F), -194.4 (dm, 5β-F); $\delta_{\rm H}$ (CDCl₃) 2.48 (m, two 4-H), 3.59 (dm, 4α-H), 5.16 (dm, 5α-H, $J_{5\alpha\rm H-5\beta\rm F}$ 49.3), 6.94 (t, 3-H); $\nu_{\rm max}$ 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%); $\delta_{\rm F}$ (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); $\delta_{\rm H}$ (CDCl₃) 5.40 (s, H_a), 5.54 (dd, H_b, $J_{\rm Fa-Hb}$ 32, $J_{\rm Ha-Hb}$ 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; $\nu_{\rm max}$ 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 C_6F_5 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 19:28.5:0.5:35:4.5:7.

(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: $C_9H_7F_5O_2$ · $^{1}_2H_2O$, 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, $\beta = 105.44(2)^{\circ}$, U = 1806(1) Å³, Z = 8 (H₂O on axis 2), $D_{calc} = 1.85$ g cm⁻³, SMART CCD area detector, Mo-K α radiation, SHELXL97 software, 6231 reflections ($2\theta \le 55^{\circ}$), 2064 unique, R = 0.034 [1703 data with $F^2 \ge 2\sigma(F^2)$], $wR(F^2) = 0.088$. 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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