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Pyrolysis reactions of 4-methyl-tetrafluorophenyl and pentafluorophenyl prop-2-enyl ethers: isomeric tetrahydroinden-1-ones from *both* intra-molecular Diels–Alder adducts of the Claisen rearrangement reaction from the 4-Me derivative

Mechanistic implications of a *thermal* retro $\pi 4s + \pi 2s$ reaction of *one* of the adducts and recyclisations by $\pi 4s + \pi 2s$ and/or $\pi 2s + \pi 2a$ routes

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Abstract

Heating 4-methyl-tetrafluorophenyl prop-2-enyl ether **16** in vacuo at 170 °C gives a mixture of products which includes 3-methyl-2,4,5,7-tetrafluorotricyclo[3.3.1.0^{2,7}]non-3-ene-6-one 18, the product of one of the two possible intra-molecular Diels–Alder reactions of the Claisen rearrangement intermediate **17**. The product of the second intra-molecular Diels–Alder reaction, **22**, is proposed as the intermediate in the formation of 6-methyl-2,5β,7,7aβ-tetrafluoro-3aβ,4,5,7a-tetrahydroinden-1-one **23** in low yield (4%) in the flash vapour phase (FVP) pyrolysis of **16** at 410 °C; the major product is 7-methyl-2,5β,6,7aβ-tetrafluoro-3aβ,4,5,7a-tetrahydroinden-1-one **27** (38%) which is the same as **23** but with the 6-Me and 7-F substituents interchanged. The facile formation of this unpredictable product is rationalised as proceeding by a retro Diels-Alder reaction of **18** to the tethered 3-methyl-2,4,5-trifluoro-2,4-cyclohexadienylmethyl fluoroketene **24** which has a choice of two intra-molecular recyclisations (by another $\pi 4s + \pi 2s$ Diels-Alder reaction to **25** skeletally identical with **22**, and/or a $\pi 2s + \pi 2a$ route to **26**) both products reacting further to **27**. Under FVP conditions at 400 °C, pentafluorophenyl prop-2-enyl ether 1 (R=F) gives 1,2,3,4,6-pentafluorotricyclo[4.3.0.0^{2,8}]non-3-ene-5-one **33** (3%), the basic structure of which is found in **26**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Claisen rearrangement; Diels-Alder adducts; Retro Diels-Alder products; $\pi 4s + \pi 2s$ and/or $\pi 2s + \pi 2a$ cyclisations; 2,4,5-Trifluoro-3-(substituent)-2,4-cyclohexadienylmethyl fluoroketene; Cycloaddition; Tricyclo[4.3.0.0^{2,8}]non-3-ene-5-one; X-ray crystal structures

1. Introduction

Pentafluorophenyl and some 4-substituted-tetrafluorophenyl prop-2-enyl ethers **1** have been shown on heating to give **3**, one of the two possible types of intra-molecular Diels-Alder adduct via the Claisen rearrangement intermediates **2**—the result of electronically favourable conditions whereby electron-poor fluorine-containing diene moieties interact with the electron-rich alkene in the same molecule [1–3]. Moreover, each of these Diels-Alder products is accompanied by its skeletally rearranged isomer **5** *via* conjugatively-stabilised diradical species **4** [2–4]; the strained cyclobutanone derivatives readily formed 1,1-diols **6** in three cases (Scheme 1).

The intermediacy of the *alternative* type of Diels–Alder adduct **7** from the pentafluorophenyl ether **1** via **2** (R=F) was first proposed in 1974 to account for the formation of the pentafluorohydroinden-1-one derivative **9** (R=F) *via* another resonance stabilised diradical **8** by flash vapour-phase pyrolysis (FVP) through a silica tube packed with silica wool carried out at 480 °C at low pressure (Scheme 2) [5]. However, when the 4-pentafluorophenyl-tetrafluorophenyl ether **1** (R=C_6F_5) was pyrolysed, the expected analogue of **9** (R=C_6F_5) was *not* the product isolated: what was isolated was the hydroinden-1-one isomer **10** (R=C_6F_5) in which the 7-F and the 6-C_6F_5 group in **9** were interchanged [2]; from compounds **1** (R=C_6H_5 and CF_3) were isolated the unexpected isomers **10** (R=C_6H_5 and CF_3) and of course, **10** is

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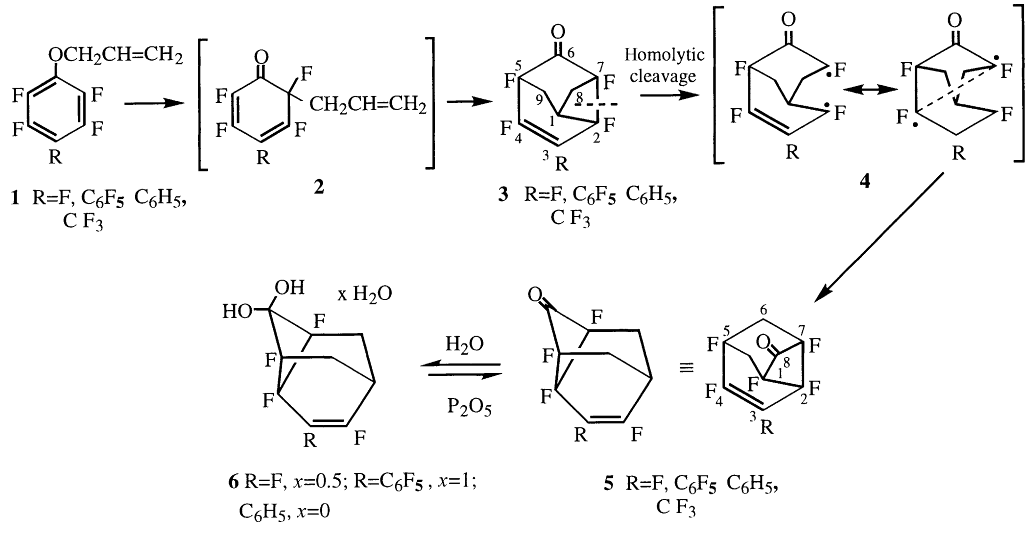
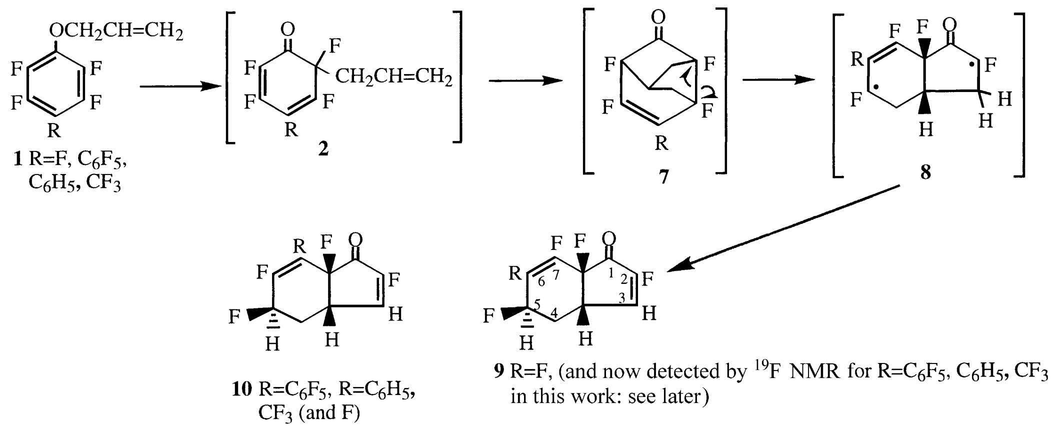


Scheme 1.



Scheme 2.

indistinguishable from **9** for R=F [5]. A remarkable departure from the expected course of reaction had obviously occurred!

Two rationalisations for the formation of compounds of structure **10** have been proposed.

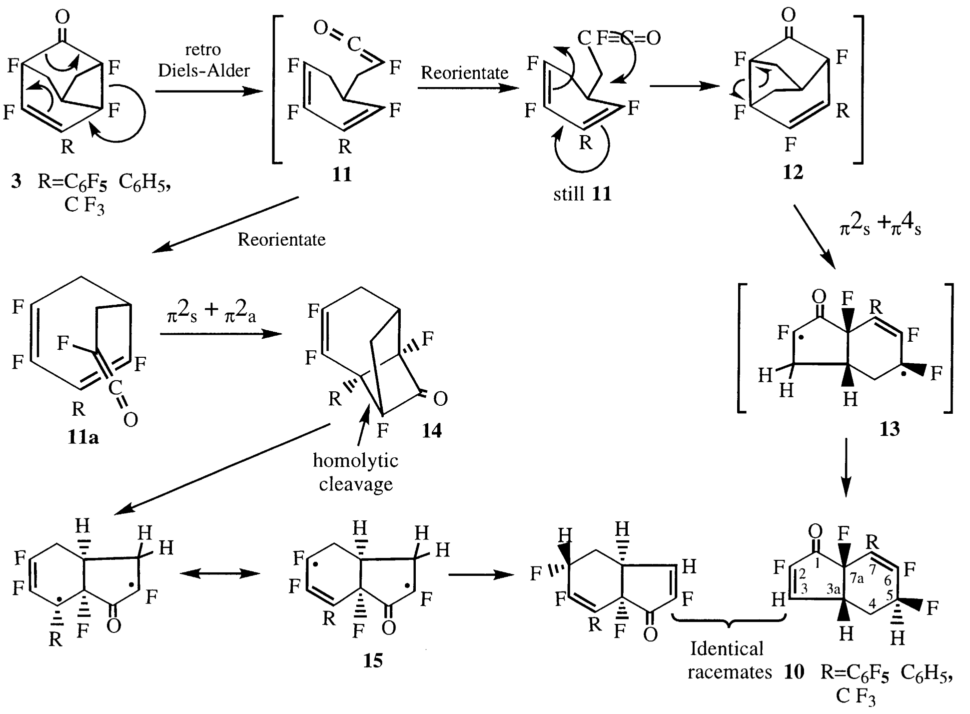
(i) Compound **12**, isomeric with and having the same carbon skeleton as **7** was the obvious precursor, which underwent ring opening to **13** and hydrogen abstraction as before (Scheme 3). The formation of the *unexpected* intermediate tricyclic compound **12** was rationalised by invoking, apparently for the first time [6,7], a retro Diels–Alder reaction of the internal Diels–Alder adduct **3** to give the cyclohexa-2,4-dienylmethyl fluoroketene **11**, followed by the *alternative* Diels–Alder cyclisation as shown in Scheme 3. It was noted that although these latter $\pi 4s + \pi 2s$ reactions are uncommon, one intra-molecular process has been recorded [8].

(ii) The second possible explanation for the formation of **10** was the intra-molecular reaction of the fluoroketene and alkene moieties in **11** to give **14** *via* the well established concerted $\pi 2s + \pi 2a$ route [9], which must then undergo radical fission to **15**, the precursor to **10** [3] (Scheme 3).

In the present paper, we report further attempts to gain concrete evidence for one or both of the proposed mechanism(s). We have looked for key intermediates of the type **11**, **12** and **14** which might accompany the rearrangement product **10** for R=CH_3 and R=F by investigating the pyrolysis reactions of 4-methyl-tetrafluorophenyl prop-2-enyl ether **16** (equivalent to **1** R=CH_3) and re-examining that of pentafluorophenyl prop-2-enyl ether **1** (R=F), respectively.

2. Results and discussion

The 4-methyl ether **16** was prepared from 4-methyl-tetrafluorophenol [10] by reaction with prop-2-enyl bromide/K_2CO_3. Firstly, a static thermolysis of **16** was carried out by heating *in vacuo* at170 °C for 94 h. Chromatography



Scheme 3.

of the product ultimately led to four components of interest: (i) the internal Diels–Alder adduct **18** (equivalent to **3**, R=CH_3) (15%), the structure of which was determined by X-ray crystallography (Fig. 1); (ii) the ketone **19** (2%) (equivalent to **5**, R=CH_3); (iii) the 8,8-diol hemihydrate **20** (3%) (equivalent to **6**, R=CH_3); and (iv) the *endo* ethoxyhemiacetal **21** (3%), the structure of which was determined by X-ray crystallography (Fig. 2). Compound **20** crystallised from water as a mixture of phases with different degrees of hydration. The better-formed crystals, suitable for X-ray crystallography, were characterised as the sesquihydrate (**20**, $x = 1.5$) (Fig. 3), although the elemental analysis and ^{1}H NMR spectrum of the bulk material corresponds very closely to the hemihydrate, as indeed did **6** (R=F) earlier [2,4]. The presence of the small proportions of **20** and **21** in the crude product must have arisen from the reaction of compound **19** present with water and with adventitious ethanol, respectively, in the solvent used in the isolation procedure. Recrystallisation of mixtures of **19** and **20** from water gave **20** while the latter on dehydration with P_2O_5 gave **19**. These results are summarised in Scheme 4.

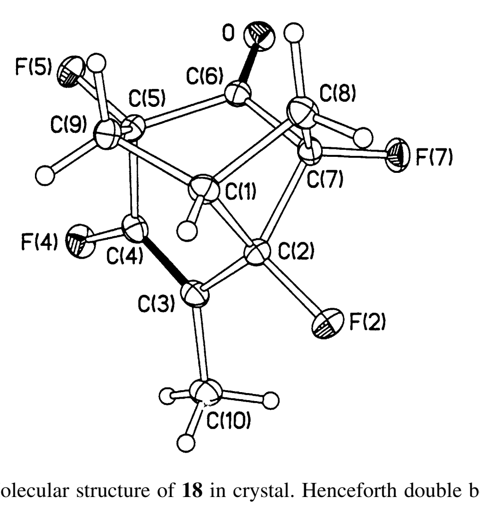


Fig. 1. Molecular structure of **18** in crystal. Henceforth double bonds are shown in black, thermal ellipsoids at 50% probability levels.

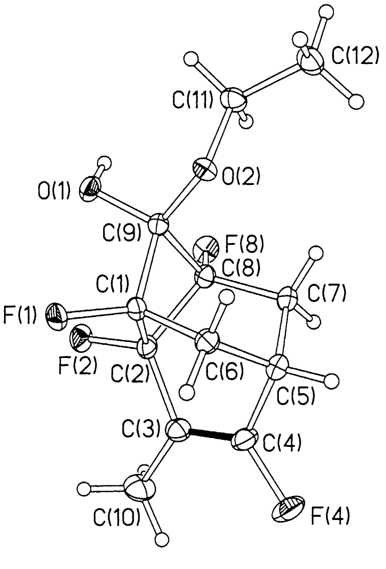


Fig. 2. Molecular structure of **21**.

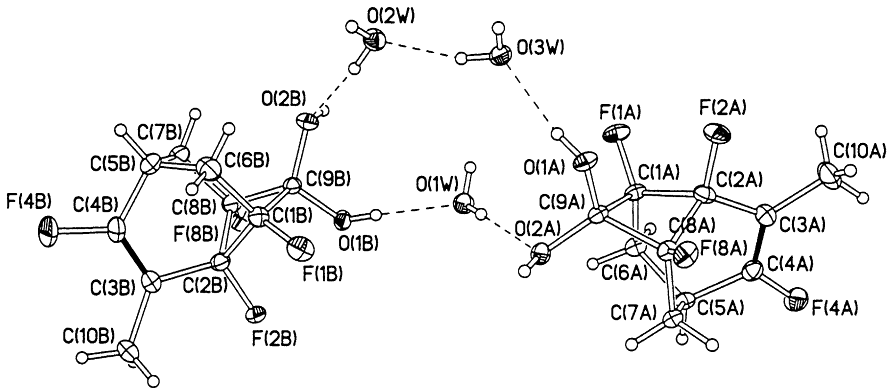
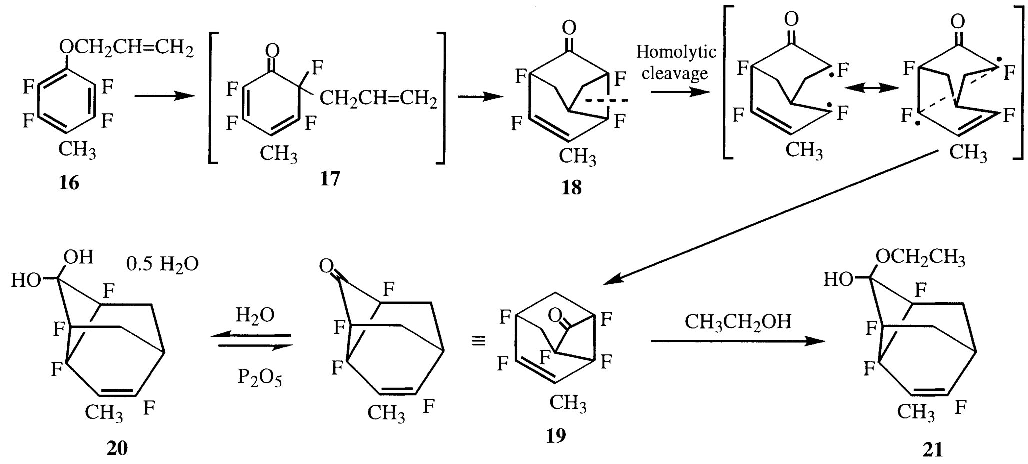


Fig. 3. Asymmetric unit of **20**·1.5H_2O, comprising 2 molecules of **20** and 3 of water (hydrogen bonds are shown as - - -).



Scheme 4.

Compound **16** was subjected to FVP at 410 °C and 0.01 mmHg as before and benzotrifluoride was added to the crude product as an internal standard to enable the yields of subsequently identified components to be determined by ^{19}F NMR spectroscopy. Of particular interest in this investigation was the possible presence of compounds having resonances at very low frequencies—shifts more negative than −200 ppm as found in the intra-molecular Diels–Alder adduct **18** (−202.5 ppm for 2-F)—shifts expected in compounds **12/14**. Compound **18** was present (0.2%) as was its rearrangement product **19** (0.1%), but there were other tantalising resonances at −202.3 and −207.8 ppm (both ca. 0.25%) in materials which were never ultimately isolated. Two compounds only were separated by chromatography on silica. The minor component, a solid, was the "expected" tetrahydroinden-1-one derivative **23** (equivalent to **9**, R=CH_3) (4%), the structure of which was determined by X-ray crystallography (Fig. 4). The major component once again was the "unexpected" tetrahydroinden-1-one derivative **27** (equivalent to **10**, R=CH_3) (38%), a liquid, the structure of which was determined by a proton decoupled ^{19}F NMR experiment; this produced a much simplified spectrum which established that the connectivities (*and* the magnitudes of the various J_{F-F}) were the same as those found in **10** (R=C_6F_5, C_6H_5 and CF_3) [2,3]. Also present in the pyrolysis product was 4-methyl-tetrafluorophenol (18%) formed from **16** by a disproportionation reaction. These results are shown in Scheme 5 which shows the two possible modes of formation of **27** via **24** and **25** and/or **26**—by analogy with Scheme 3.

The conclusion drawn *from this work* is that the isolation of the tetrahydroinden-1-one derivative **23** from **16** (the first example of the "expected" compound to be detected and

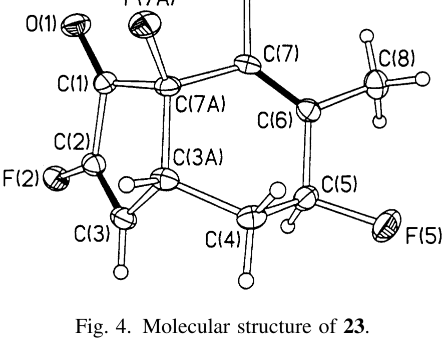
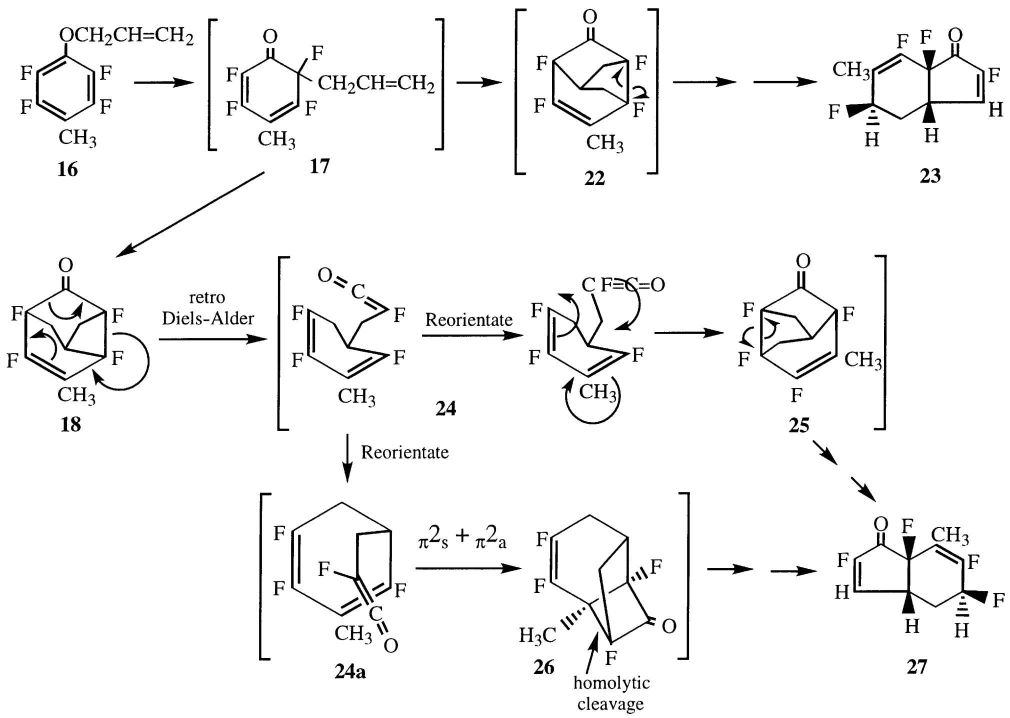


Fig. 4. Molecular structure of **23**.



Scheme 5.

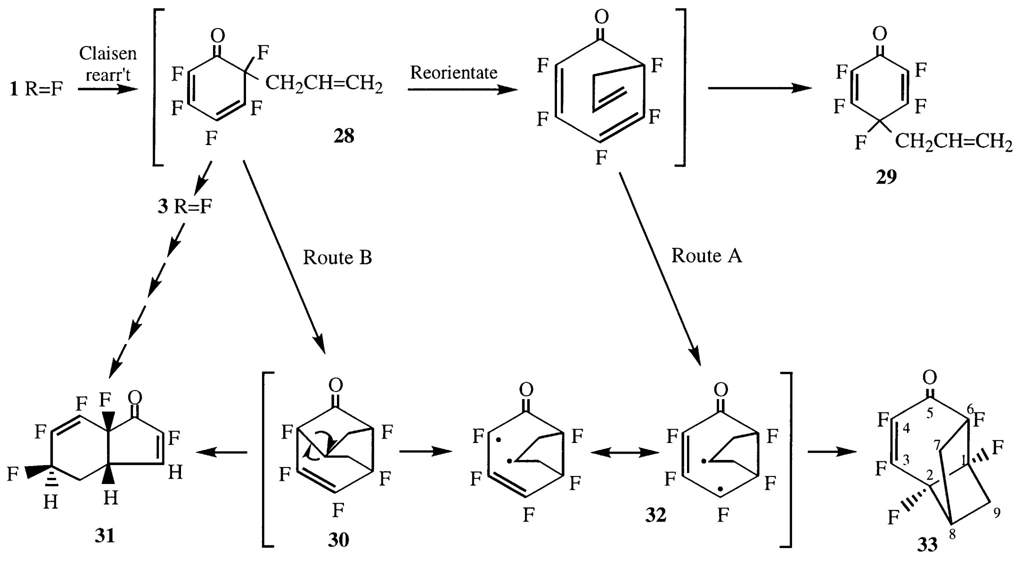
isolated in this area of chemistry) *does* show that the original proposal with the reaction proceeding *via* the simple intramolecular Diels–Alder addition product **22** (7 in Scheme 2 for R=CH_3) from the Claisen rearrangement product **17**, is perfectly reasonable, but that there is a much easier route to the tetrahydroinden-1-one isomer **27** (equivalent to **10** R=CH_3), two plausible pathways being shown above.

Not having found any key intermediates of the type **11**, **12** and **14** which might have accompanied the formation of the tetrahydroinden-1-one derivatives **23** and **27** in the pyrolysis reaction of 4-methyl-tetrafluorophenyl prop-2-enyl ether **16**, attention was turned to a reinvestigation of work carried out originally with pentafluorophenyl prop-2-enyl ether **1** (R=F) [5,11], particularly since NMR facilities have advanced enormously in the past 25–30 years. The ether **1** (R=F) was pyrolysed at 400 °C and 0.01 mmHg and the crude product with added benzotrifluoride as internal standard was examined by ^{19}F NMR spectroscopy. Five products were readily identified: the Claisen/Cope rearrangement product 4-[prop-2-enyl]-2,3,4,5,6-pentafluoro-2,5-cyclohexadienone **29** [11] (35%) and the pentafluorohydroinden-1-one derivative **31** [5] (20% yield) (Scheme 6); and very small amounts of the intra-molecular Diels–Alder adduct **3** (R=F) (0.5%) [1], and the rearrangement product of **3**, namely **5** (R=F) (0.1%) [4] accompanied by its 1,1-diol hemihydrate **6** (R=F) (0.15%) [4], (Scheme 1). However, of particular interest in the low frequency region of the spectrum was a material having resonances at −180.5, −180.8 and −209.5 ppm in the ratio 1:1:1, present in ca. 3% yield. This compound was isolated from the complex mixture by chromatography and sublimation to give **33**, the structure of which was determined by X-ray crystallography (Fig. 5). Two routes to **33** *via* the Claisen rearrangement intermediate **28** can be envisaged: (i) route A by a direct formation of the four membered ring with the substituted hydrocarbon ethene moiety of the prop-2-enyl group at C-2 of the ring, appropriately orientated, undergoing a cycloaddition reaction with the 3,4-difluoro alkene moiety of the cyclic conjugated diene, a reaction type which is peculiar to fluorocarbon chemistry proceeding in a stepwise way via the diradical **32** [12]; (ii) route B involves the intra-molecular Diels–Alder adduct having the structure **30** which also cleaves homolytically and rearranges *via* the same diradical **32**, Scheme 6. However, it is not possible to distinguish between these two possibilities.

Compound **33** possesses the rare tricyclo[4.3.0.0^{2,8}]nonane ring structure. Closely related structures have been formed by the photochemical cyclisations of 4-methyl-4-[prop-2-enyl]-cyclohex-2-enone and 5-methyl-5-[prop-2-enyl]-cyclohex-2-enone [13].

The particularly interesting structural feature of compound **33** is that it has the same carbon skeleton as the intermediates **14** proposed earlier [3] when it was also observed from molecular models that the orientation of tethered fluoroketene **11a** (and now in this work, **24a**) required for the $\pi 2s + \pi 2a$ cycloaddition reactions are favourable, even though the adducts are highly strained (Scheme 3). Structure **33** lends *some* credence, therefore, to the viability of the mechanism in which **14** and **26** are invoked.

To summarise the present work leading to tetrahydroinden-1-one derivatives in the wider context of previous investigations, the following points can be made.



Scheme 6.

1. The isolation of **23** (4% yield) from the pyrolysis of **16** shows that the *simple* intra-molecular Diels–Alder adduct **22** must be involved as an *intermediate*, even though its formation is not favoured.
2. Compound **27** (36% yield), isomeric with **23**, is formed more readily from **16**, but from the other ethers **1** (R=C_6F_5, C_6H_5 and CF_3) only materials analogous to **10** were isolated. However, in the light of the present work, a re-examination of the ^{19}F NMR spectra of the crude products from the pyrolyses of these compounds indicates that relative to the *surprise* products **10** (100 parts), the *expected* isomers **9** can now be seen to be formed in smaller proportions from intramolecular Diels–Alder adducts of general structure **7** (27.5, 12 and 78 parts for R=C_6F_5, C_6H_5 and CF_3 respectively).
3. The tethered tetrafluorocyclohexa-2,4-dienylmethyl fluoroketene **24** and related compounds **11** are *pre-requisites* for the mechanisms proposed to produce **27** and **10**, respectively, in these reactions. The simple intra-molecular Diels–Alder adducts **18** and **3**, which are stable, characterised compounds, must undergo the alternative retro Diels–Alder reaction to form the tethered fluoroketene. These thermal reactions (as opposed to photochemical reactions [6,7]) are to our knowledge, the first examples of this type of reaction.
4. The final pathway from tethered fluoroketene to rearranged tetrahydroinden-1-one derivatives is ambiguous but the intermediacy of $\pi^2s + \pi^2a$ addition products **14** and **26** have become even more plausible with the isolation of **33** having the same basic skeleton from the related reaction involving **3** (R=F).

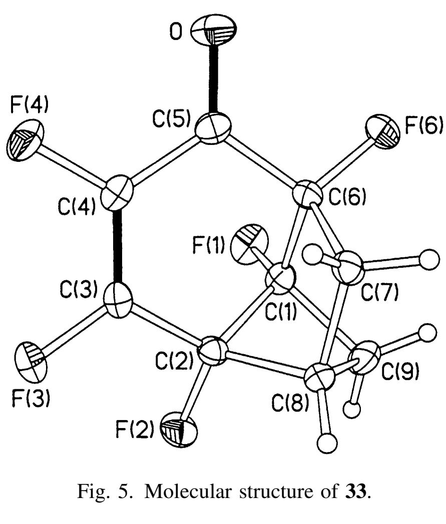


Fig. 5. Molecular structure of **33**.

Intra-molecular Diels–Alder adducts of type **3** in general (including R=CH_3, i.e. **18**), available only because of the electronic properties of fluorine, have enabled a general area of chemistry to be opened up (intra-molecular retro Diels–Alder reactions to ketenes and dienes) in the deductive sense—in the way that Kimball and Roberts first proposed the existence of bromonium ions to account for the stereoselectivity of bromine addition to alkenes [14], their existence only to be proved many years later by the classical work of Olah and Bollinger [15].

Compound **23** has not rearranged to **27**; rather, a different series of reactions have occurred. The wondrous thing about Nature is that the shorter three step process from **17** (and analogous intermediates **2**) is in fact more difficult than the longer five step process from **17**!

3. Experimental

NMR spectra were recorded on the following instruments at the frequencies listed: Varian Mercury 200 (^{1}H, 199.991 MHz; ^{19}F, 188.179 MHz) and Varian Inova 500 (^{1}H, 499.782 MHz; ^{19}F, 470.262 MHz). Chemical shifts are reported using the high-frequency positive convention from TMS and CFCl3, hence ^{19}F resonance values are negative; *J* values are in Hz); ^{19}F COSY/proton decoupled experiments were carried out on compounds **23**, **27** and **33** to establish connectivities. Elemental analyses were performed on an Exeter Analytical Inc CE440 elemental analyser.

3.1. Preparation of 4-methyl-tetrafluorophenyl prop-2-enyl ether *16*

A mixture of 4-methyl-tetrafluorophenol [10] (30.95 g), allyl bromide (26.34 g), and potassium carbonate (29.8 g) in acetone (130 ml) was heated under reflux for 21 h, filtered, the solvent removed in vacuo at room temperature and the residue distilled to give 4-methyl-tetrafluorophenyl prop-2-enyl ether **16** (27.8 g, 73%), bp 83 °C at 10 mmHg (Found: C, 54.18; H, 3.62. $C_{10}H_8F_4O$ requires: C, 54.56; H, 3.66%); δ_F ($CDCl_3$) −145.6 (dd, 3-F, 5-F), −158.3 (dd, 2-F, 6-F); δ_H ($CDCl_3$) 2.20 (4-CH_3), 4.67 (d, CH_2), 5.25, 5.32, 5.40 (2 overlapping d, $C\underline{H}_2$=CH), 6.02 (m, CH_2=C$\underline{H}$).

3.2. Static thermolysis of 4-methyl-tetrafluorophenyl prop-2-enyl ether *16*

The ether **16** (4.615 g) was sealed in a 10 l round-bottomed flask in vacuo and heated at 170 °C for 94 h. The products were condensed into a side arm cooled in liquid air, washed from the opened vessel with ether which must have contained some adventitious ethanol resulting in the formation of **21** (see later) and the solvent evaporated to give the crude product (2.30 g) the ^{19}F NMR of which showed a complex mixture of products once again. Chromatography of the crude product on silica using diethyl ether/light petroleum (bp 40–60 °C) (40:60% v/v) as eluant gave fractions which were examined by ^{19}F NMR spectroscopy. Three compounds of interest were identified in fractions eluting from the column: (i) some earlier fractions (0.145 g, 3% of the starting material) contained crystals which were washed with cold light petroleum (bp 40–60 °C) and then recrystallised from light petroleum (bp 60–80 °C) and sublimed at 52° at 0.01 mmHg to give *3*-methyl-1,2,4,7-tetrafluorotricyclo[3.3.1.0^{2,7}]non-3-ene-8-endoethoxy-8-ol **21** mp 62–66 °C, the ^{19}F NMR of which showed the presence of 3% of compound **20** (Found: C, 53.98; H, 5.32. $C_{12}H_{14}F_4O_2$ requires: C, 54.14; H, 5.30%); δ_F($CDCl_3$) −115.6 (s, 4-F), −193.0 (dm, 1-F, 7-F), −205.0 (s, 2-F); δ_H($CDCl_3$) 1.25 (t, $C\underline{H}_3CH_2$), 1.56 (overlapping d, 2 unassigned H), 1.74 (t, 4-CH_3), 2.39 (m, 2 unassigned H), 2.67 (m, 1H), 3.35 (d, 1 unassigned H), 3.74 (t, $CH_3C\underline{H}_2$); υ_{max} 3413 (O–H), 1717 cm^{-1}. (ii) The next fractions of interest (0.679 g, 15% of the starting material) were recrystallised from light petroleum (bp 40–60 °C)/diethyl ether to give 3-methyl-2,4,5,7-tetrafluorotricyclo[3.3.1.0^{2,7}]non-3-ene-6-one **18** mp 65.0–65.5 °C (Found: C, 54.43; H, 3.63. $C_{10}H_8F_4O$ requires: C, 54.55; H, 3.66%); δ_F($CDCl_3$) −135.3 (s, 4-F), −176.2 (m, 7-F), −194.5, (m, 5-F), −202.5 (d, 2-F); δ_H($CDCl_3$) 1.83 (t, 3-CH_3), 2.01 (dd, 1H), 2.19 (m, 1H), 2.85 (m, 1H), 3.15 (m, 1H); υ_{max} 1775 (C=O), 1698[C(CH_3)=CF] cm^{-1}. (iii) The slowest eluting fractions (0.238 g, 5% of the starting material) contained mainly two components **19** and **20** in the ratio of 2:3, respectively. Recrystallisation of the mixture from water gave *3*-methyl-1,2,4,7-tetrafluorotricyclo[3.3.1.0^{2,7}]non-3-ene-8,8 diol hemihydrate **20** (equivalent to **6**, R=CH_3, *x* is 0.5) mp 65–70 °C (Found: C, 48.36; H, 4.05. $C_{10}H_{11}F_4O_{2.5}$ requires: C, 48.59; H, 4.48%); δ_F($CDCl_3$) −115.9 (m, 4-F), −195.9 (d, 1-F, 7-F), −205.9 (s, 2-F); δ_H($CDCl_3$) 1.59 (t, 3H), 1.75 (t, 3-CH_3), overlapping multiplets from 2.40 to 2.88 (4H), 3.82 (broad s, 1H); υ_{max} 3334 (shoulders at 3586, 3527) (gem-diol and unknown amount of water of crystallisation), 1716 [C(CH_3)=CF] cm^{-1}. Sublimation of a mixture of 20 and P_2O_5 at 50–60 °C/0.01 mmHg gave 3-methyl-1,2,4,7-tetrafluorotricyclo[3.3.1.0^{2,7}]non-3-ene-8-one **19** (equivalent to R=CH_3) mp 70.5–76 °C (Found: C, 54.44; H, 3.65. $C_{10}H_8F_4O$ requires: C, 54.56; H, 3.66%); δ_F($CDCl_3$) −115.2 (m, 4-F), −188.1 (d, 1-F, 7-F), −205.4 (m, 2-F); δ_H($CDCl_3$) 1.87 (t, 3-CH_3), overlapping multiplets from 1.90 to 2.13 (2H), 2.45 and 2.51 (overlapping m, 2H), 2.88 (dm, 1H); υ_{max} 1825 (C=O), 1713 cm^{-1} [C(CH_3)=CF].

3.3. FVP of 4-methyl-tetrafluorophenyl prop-2-enyl ether *16* at 410 °C

Over a period of 3.75 h, the ether **16** (15.115 g) was distilled in vacuo (initially at 0.01 mmHg) from a flask heated in a water bath at ca. 60 °C through a silica tube (510 mm × 20 mm) packed in the middle 170 mm with silica wool and heated in an oven at 410 °C, the products of pyrolysis being collected in a trap cooled in liquid nitrogen; the maximum pressure recorded during the experiment was 0.15 mmHg. To the (liquid) pyrolysate (14.16 g), was added benzotrifluoride (0.252 g) as an internal standard for ^{19}F NMR spectroscopic determination of the yields of the materials which were subsequently identified in the complex mixture of compounds. Chromatography of the crude product on silica (750 g) using diethyl ether/light petroleum (bp 40–60 °C) (40:60% v/v) as eluant gave fractions which were examined by ^{19}F NMR spectroscopy. Two components of interest were identified in fractions from the column: (i) a liquid product (3.67 g) isolated by distillation into a cup at the end of a water-cooled finger at 0.005 mmHg/40 °C was 7-methyl-2,5β,6,7aβ-tetrafluoro-3aβ,4,5,7a-tetrahydroinden-1-one **27** (Found: C, 54.43; H, 3.62. $C_{10}H_8F_4O$ requires: C, 54.56; H, 3.66%); δ_F($CDCl_3$) −113.7 (d, 6-F; $J_{5\beta F-6F}$ 23.7; $J_{6F-7a\beta F}$ 3.6), −135.7 (d, 2-F; J_{2F-3H} 7.3, $J_{2F-7a\beta F}$ 2.15), −155.0 (m, 7aβ-F; $J_{5\beta F-7a\beta F}$ 8.6), −189.7 (dm, 5β-F); δ_H($CDCl_3$) 1.88 (m, 7-CH_3), 2.12 (m, 1 unassigned H), 2.38 (m, 1 unassigned H), 3.32 (dm, 1 unassigned H), 4.92 (dm, 5a-H; $J_{5aH-5\beta F}$ 50.4), 6.89 (m, 3H); υ_{max} 3088 (=C–H), 1744 (C=O), 1703 [C(CH_3)=CF] and 1652 cm^{-1} (CF=CH); and a slower moving component (0.155 g); and

(ii) 6-methyl-2,5β,7,7aβ-tetrafluoro-3aβ,4,5,7a-tetrahydroinden-1-one **23** mp 79.5–81 °C (from cyclohexane-toluene) (Found: C, 54.35; H, 3.63. $C_{10}H_8F_4O$ requires: C, 54.56; H, 3.66%); $\delta_F(CDCl_3)$ −129.2 (d, 7-F; $J_{5\beta F-7F}$ 2.9; $J_{7F-7a\beta F}$ 29.4), −132.8 (d, 2-F; J_{2F-3H} 8.3, $J_{2F-7a\beta F}$ 2.15), −168.0 (m, 7aβ-F; $J_{5\beta F-7a\beta F}$ 6.8), −186.9 (dm, 5β-F); $\delta_H(CDCl_3)$ 1.85 (t, 6-CH_3), 2.16 (m, 1 unassigned H), 2.33 (m, 1 unassigned H), 3.44 (dm, 1 unassigned H), 4.83 (dm, 5a-H; $J_{5aH-5\beta F}$ 49), 6.85 (m, 3H); υ_{max} 3064 (=C–H), 1747 (C=O), 1703 [C(CH_3)=CF] and 1639 cm^{-1} (CF=CH).

The ^{19}F NMR spectrum of the crude reaction product containing the internal standard ($C_6H_5CF_3$) showed the presence of unreacted prop-2-enyl ether **16** (0.499 g), which indicated that 14.616 g (15.115–0.499 g) (97%) had been converted to products. Other components in the mixture in addition to the isomeric tetrahydroinden-1-one isomers **23** and **27** were the internal Diels–Alder adduct **18**, its 1,3-rearrangement product **19** and 4-methyl-tetrafluorophenol, with yields (based on the 14.616 g of ether **16** consumed) of 4, 38, 0.2, 0.1 and 18%, respectively.

*3.4. FVP of pentafluorophenyl prop-2-enyl ether **1** (R=F) at 400 °C*

The ether **1** (R=F) [5] (12.264 g) was pyrolysed as in Section 3.2 over 1.75 h to give 12.08 g of product; to this was added benzotrifluoride (0.225 g) as the internal standard. The ^{19}F NMR was complex, but of particular interest was the presence of an unknown compound having low frequency resonances at ca. −180.5, −180.8 and −209.5 ppm in the ratio 1:1:1 indicative of fluorines at bridgehead sites (compound **33**), and the tetrahydroinden-1-one derivative **31**. A second smaller scale pyrolysis reaction of **1** (R=F) (3.329 g) under similar conditions gave further pyrolysate (3.27 g), and 15.35 g of the combined materials was separated by chromatography on silica (750 g) using diethyl ether/light petroleum (bp 40–60 °C) (40:60% v/v) as eluant. Fractions were examined by ^{19}F NMR spectroscopy, one of which contained **31** and **33** (1.0 g) which was sublimed at ca. 50 °C/0.01 mmHg and the sublimate (0.9 g) re-chromatographed on silica (95 g) with diethyl ether/light petroleum (bp 40–60 °C) (30:70% v/v) as eluant. Greatly enriched fractions of **33** (0.19 g) were slowly sublimed at 33 °C/0.01 mmHg to give the pure crystalline 1,2,3,4,6-pentafluorotricyclo-[4.3.0.$0^{2,8}$]non-3-ene-5-one **33** mp 51–52.5 °C (sealed tube) (Found: C, 48.03; H, 2.16. $C_9H_5F_5O$ requires: C, 48.23; H, 2.25%); $\delta_F(CDCl_3)$ −127.1 (m, 3-F; J_{1F-3F} 16.1; J_{3F-4F} 7.5), −153.2 (m, 4-F; J_{4F-6F} 10.8), −180.5 (m, 6-F; J_{1F-6F} 6; J_{2F-6F} 6), −180.7 (d, 2-F; J_{1F-2F} 2; J_{2F-3F} 2), −209.5 (m, 1-F; J_{1F-4F} 2.5); $\delta_H(CDCl_3)$ 2.23 (m, 1H), 2.32 (complex d, 1H), 2.38 (complex m, 1H), 3.02 (m, 1H), 3.15 (complex d, 1H); υ_{max} 1728 (C=O), 1692 cm^{-1} [CF=CF].

The ^{19}F NMR spectrum of the pyrolysate from 12.264 g ether **1** (R=F) containing the internal standard showed unreacted ether **1** (1.281 g). Based on the amount of ether **1** consumed (10.983 g) the yields of the tetrahydroinden-1-one **31** and the tricyclo[4.3.0.$0^{2,8}$]non-3-ene-5-one **33** were 20 and 3%, respectively. Three other known compounds identified for R=F (in very low yields) were: **3** (0.5%), **5** (0.1%) and **6** (0.15%), but the major product was the 2,5-cyclohexadienone **24** (35%); there was no C_6F_5OH.

Table 1
Crystal data and experimental details

	Compound				
	18	**20**	**21**	**23**	**33**
Formula	$C_{10}H_8F_4O$	$C_{10}H_{13}F_4O_2 \cdot 1.5H_2O$	$C_{12}H_{14}F_4O_2$	$C_{10}H_8F_4O$	$C_9H_5F_5O$
Formula weight	220.16	265.20	266.23	220.16	224.13
T (K)	102	100	102	100	100
Symmetry	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	*Pbca* (no. 61)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a (Å)	5.8604(5)	6.712(1)	11.980(3)	6.463(1)	6.715(1)
b (Å)	12.096(1)	11.041(2)	7.274(2)	7.338(1)	10.753(1)
c (Å)	24.321(2)	15.542(5)	13.443(3)	18.659(3)	11.513(3)
α (°)	90	98.89(1)	90	90	90
β (°)	90	90.51(1)	100.01(1)	90	90
γ (°)	90	95.05(1)	90	90	90
V ($Å^3$)	1724.0(3)	1133.2(3)	1153.6(5)	884.9(2)	831.3(3)
Z	8	4	4	4	4
Crystal size (mm^3)	0.12 × 0.40 × 0.65	0.07 × 0.12 × 0.55	0.15 × 0.5 × 0.8	0.09 × 0.12 × 0.9	0.05 × 0.1 × 0.3
Reflections total	9991	13915	13435	5768	10104
Reflections unique	2195	5921	3038	1425 (2371[a])	1292 (2196[a])
Reflections $I > 2\sigma(I)$	2005	4625	2804	1320 (2197[a])	1239 (2121[a])
$R[I > 2\sigma(I)]$	0.033	0.043	0.033	0.030	0.025
$\omega R(F^2)$, all data	0.090	0.119	0.092	0.076	0.071
CCDC deposition no.	163778	163779	163780	163781	163782

[a] Including Friedel equivalents.

*3.5. Re-examination of the ^{19}F NMR spectra of the crude reaction products from the pyrolyses of the prop-2-enyl ethers **1** (R=C_6F_5 [2], C_6H_5 [3] and CF_3 [3])*

The following compounds having structure **9** were detected: (i) for R=C_6F_5, $\delta_F(CDCl_3)$ −112.0 (d, 7-F; $J_{7F-7a\beta F}$ 30.3), −130.9 (d, 2-F; J_{2F-3H} 8.3), −167.1 (m, 7aβ-F), −182.9 (dm, 5β-F; $J_{5\alpha H-5\beta F}$ 49), **9** : **10** = 27.5 : 100; (ii) for R=C_6H_5, $\delta_F(CDCl_3)$ −124.7 (d, 7-F; $J_{7F-7a\beta F}$ 32.7), −134.0 (d, 2-F; J_{2F-3H} 7.1), −160.9 (m, 7aβ-F), −176.5 (dm, 5β-F; $J_{5\alpha H-5\beta F}$ 48.4), **9** : **10** = 12 : 100; and (iii) for R=CF_3, $\delta_F(CDCl_3)$ −61.5 (6-CF_3), −108.0 (m, 7-F), −134.5 (d, 2-F; J_{2F-3H} 6.4), −161.0 (m, 7aβ-F), −177.3 (dm, 5β-F; $J_{5\alpha H-5\beta F}$ 48.3), **9** : **10** = 78 : 100.

3.6. X-ray crystallography

Diffraction experiments were carried out on a SMART 3-circle diffractometer with a 1 K CCD area detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. A hemisphere (**18**, **23**) or full sphere (**20**, **21**, **33**) of reciprocal space ($2\theta \leq 58^\circ$) was covered by a combination of **4** or **5** sets of ω scans, each set at different ψ and/or 2θ angles [16]. The structures were solved by direct methods and refined by full-matrix least squares (non-H atoms anisotropic; all H located in difference Fourier map and refined isotropically) against F^2 of all data, using SHELXTL software [17]. Racemic products **23** and **33** were enantiomerically resolved on crystallisation, but the absolute structures proved undeterminable from lack of anomalously scattering atoms. Crystal data and experimental details are summarised in Table 1; full structural information has been deposited at the Cambridge Crystallographic Data Centre, deposition numbers CCDC-163778 to 163782.

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