Pyrolysis reactions of 4-nonafluorobiphenyl prop-2-enyl ether: a remarkable rearrangement reaction

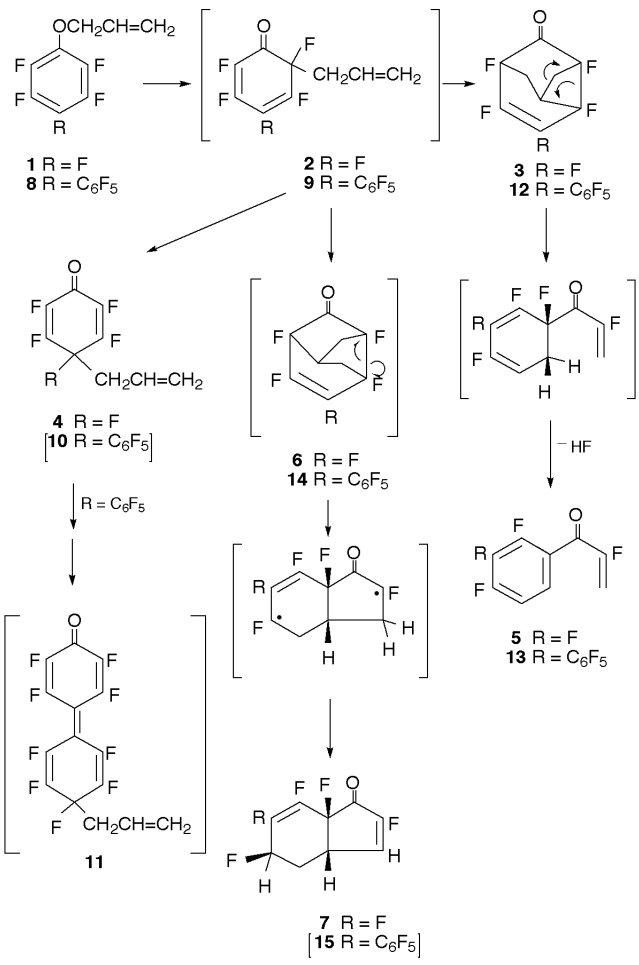
Andrei S. Batsanov, Gerald M. Brooke,* Darren Holling and Alan M. Kenwright

Chemistry Department, Science Laboratories, South Road, Durham, UK DH1 3LE.
E-mail: g.m.brooke@durham.ac.uk

Received (in Liverpool, UK) 21st April 1999, Accepted 9th July 1999

The formation of the unexpected bicyclic compound 16 *via* the pyrolytic isomerisation of 4-nonafluorobiphenyl prop-2-enyl ether 8 can be rationalised by invoking the intermediacy of a rare retro-cyclisation reaction of the internal Diels–Alder adduct 12 (from the Claisen intermediate 9) to a tethered ketene 18, recyclisation *via* the alternative mode to 17 and its subsequent transformation.

In some earlier work[1] the thermolysis of pentafluorophenyl prop-2-enyl ether **1** *in vacuo* at 137–141 °C over 13 days was shown to give **3**, one of the two possible intramolecular Diels–Alder adducts from the intermediate Claisen rearrangement compound **2**. Under FVP conditions at 365 °C and 0.05 mmHg through a silica tube packed with silica wool, **1** gave the cyclohexa-2,5-dienone **4** *via* **2** followed by a classical Cope rearrangement,[2] while under even more forcing conditions at 440 °C and 0.001 mmHg the fluorovinyl compound **5** was isolated, formed by the decomposition of **3** and loss of HF.[3] In a separate FVP experiment at 480 °C and 0.05–0.1 mmHg, **1** was also shown to be converted into the bicyclic compound **7**, the formation of which was rationalised by invoking the decomposition of the other possible intramolecular Diels–Alder adduct **6**, formed from **2**.[4] All these reactions are summarised in Scheme 1 which also shows the original objective of the present work: namely, the investigation of the pyrolysis of the closely related 4-nonafluorobiphenyl prop-2-enyl ether **8** to ascertain whether **10**, an expected intermediate from the Claisen rearrangement intermediate **9**, would undergo two further possible rearrangements to give the novel isomer **11**; to our knowledge, no Cope rearrangement has ever been described in which one moiety in a 3,3-sigmatropic reaction is an aromatic ring. In the event, no isomerisation of **8** to either **10** or **11** occurred, but a much more interesting rearrangement reaction was discovered.



Scheme 1

The starting ether **8**, readily accessible from 4-hydroxynonafluorobiphenyl,[5] was subjected to FVP at 350 °C and 0.01 mmHg as before to give a complex mixture of products among which was **12** (13% isolated yield), the structure of which was determined by X-ray crystallography† (Fig. 1). When the pyrolysis of the ether **8** was carried out at 420 °C and 0.01 mmHg, more than 90% of the crude product was shown by ^{19}F NMR spectroscopy to contain three major products in the proportions shown, which were separated by chromatography on silica using light petroleum (bp 40–60 °C)–Et_2O (95 : 5 v/v): 4-hydroxynonafluorobiphenyl (46%); the fluorovinyl compound **13** (24%) (identified unequivocally by ^{1}H, ^{19}F and ^{19}F–^{19}F COSY NMR spectroscopy); and a compound isomeric with the starting material, possessing a CHF functionality (readily identified by ^{1}H NMR spectroscopy as a doublet, $J_{H,F}$ 49 Hz) (30%). Not all of the ^{1}H and ^{19}F NMR characteristics of this latter product were in agreement with the expected bicyclic

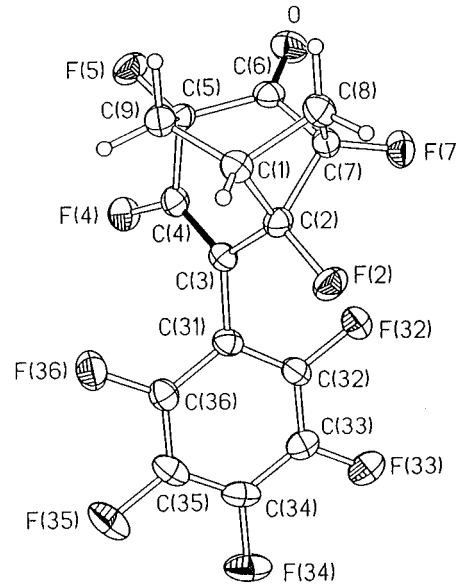


Fig. 1 Molecular structure of **12** (50% displacement ellipsoids; double bonds shown in black).

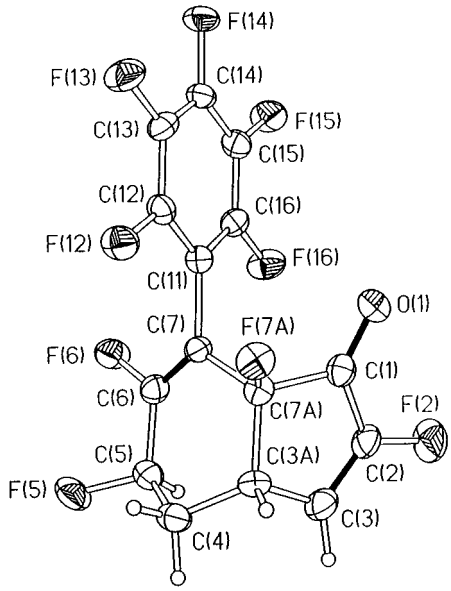
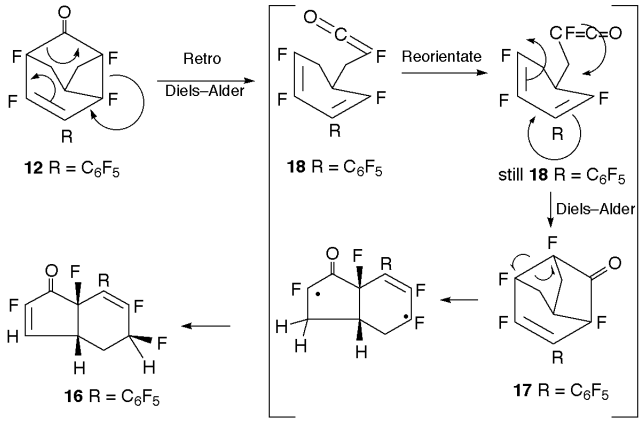


Fig. 2 Molecular structure of **16** (50% displacement ellipsoids; double bonds shown in black).

compound **15** which would have been formed if the Diels–Alder adduct **14** had been produced directly from the Claisen intermediate **9** by analogy with the mechanism proposed earlier for the formation of **7** from **1** *via* **2** and then **6**. The material was shown by X-ray crystallography† to have the structure **16** (Fig. 2) which enabled all the NMR data to be rationalised.

The formation of compound **16** (a racemate, but having the enantiomeric structure shown in Scheme 2 when formed from **12** with the configuration given), isomeric with the starting material **8**, poses an intriguing mechanistic problem since the Diels–Alder adduct **14** must not have been formed from **9** during the reaction; the precursor to **16** has to be **17**, the basic skeleton of which is identical with **14** but having the alkenic F and R groups interchanged. The formation of the unexpected intermediate tricyclic compound **17** can be rationalised most simply on the basis of a retro-Diels–Alder reaction of **12** to give the cyclohexa-2,4-dienylmethyl fluoroketene **18**—a very rare[6] reaction type—followed by the alternative intramolecular Diels–Alder cyclisation as shown in Scheme 2. Intermolecular (4 + 2) π reactions of ketenes to form six-membered *carbocyclic* rings[7] are uncommon, but an intramolecular process of this type has been recorded.[8]



Scheme 2

The present work begs the question: *why* do the complex molecular dynamics involved in the rearrangement of **12** to **17** take place in preference to the direct formation of **14** having the same basic carbon skeleton? We have no real answer to this question but models show that the formation of structures **6**[4] and **14** from **2** and **9** respectively are sterically more demanding than for the formation of compounds **3** and **12**, which were isolated under milder conditions. Consequently, even the formation of **7** is likely to proceed *via* this new molecular rearrangement reaction.

Notes and references

† *Crystal data* for **12**: $C_{15}H_5F_9O$, M = 372.2, monoclinic, space group $C2/c$ (No. 15), a = 21.242(3), b = 6.219(2), c = 20.254(2) Å, β = 93.05(1)°, U = 2671.8(8) Å, Z = 8, D_c = 1.851 g cm^{-3}, μ = 1.84 mm^{-1}, T = 150 K, 3080 reflections (2394 unique) with $2\theta \leqslant 150°$, 247 variables, R_1 = 0.037 and wR_2 = 0.098 on 1926 data with $I \geqslant 2\sigma(I)$, max. residual $\Delta\rho$ = 0.25 e Å^{-3}. For **16**: $C_{15}H_5F_9O$, M = 372.2, monoclinic, space group $P2/c$ (No. 13), a = 13.446(2), b = 11.033(1), c = 19.249(1) Å, β = 108.41(1)°, U = 2709.4(5) Å, Z = 8, D_c = 1.825 g cm^{-3}, μ = 1.81 mm^{-1}, T = 150 K, 5009 reflections (4172 unique) with $2\theta \leqslant 135°$, 492 variables, R_1 = 0.046 and wR_2 = 0.100 on 3238 data with $I \geqslant 2\sigma(I)$, max. residual $\Delta\rho$ = 0.23 e Å^{-3}. X-Ray experiments were performed on a Rigaku AFC6S 4-circle diffractometer (Cu-Kα radiation, $\bar{\lambda}$ = 1.54184 Å, $2\theta/\omega$ scan mode); structure solution (direct methods) and least-squares refinement (non-H atoms anisotropic, all H refined isotropically, against F^2 of all data) with SHELX-97 software (G. M. Sheldrick, University of Göttingen, Germany, 1997); CCDC 182/1326. See http://www.rsc.org/suppdata/cc/1999/1549/ for crystallographic data in .cif format.

1 G. M. Brooke and D. H. Hall, *J. Fluorine Chem.*, 1982, **20**, 163.
2 G. M. Brooke, *Tetrahedron Lett.*, 1971, 2377.
3 G. M. Brooke and D. H. Hall, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1463.
4 G. M. Brooke, *J. Chem. Soc., Perkin Trans. 1*, 1974, 233.
5 M. W. Buxton, R. H. Mobbs and D. E. M. Wotton, *J. Fluorine Chem.*, 1972/73, **2**, 231.
6 D. J. Pollart and H. W. Moore, *J. Org. Chem.*, 1989, **54**, 5444; T. T. Tidwell, *Ketenes*, Wiley, New York, 1995.
7 J. A. Hyatt and P. W. Raynolds, *Org. React.*, 1994, **45**, 159.
8 T. Miyashi, H. Kawamoto, T. Nakajo and T. Mukai, *Tetrahedron Lett.*, 1979, 155.

Communication 9/03209F