

## Pyrolyses of Pentafluorophenyl Prop-2-enyl and [2,3,3-<sup>2</sup>H<sub>3</sub>]Prop-2-enyl Ethers. Reactions Proceeding *via* Internal Diels–Alder Reactions

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The formation of 2,5β,6,7,7aβ-pentafluoro-3aβ,4,5,7a-tetrahydroinden-1-one (V) by the pyrolysis of pentafluorophenyl prop-2-enyl ether (I) at 480° in the vapour phase is rationalised in terms of a reaction involving one of the two possible internal Diels–Alder adducts of the intermediate 2,3,4,5,6-pentafluoro-2-(prop-2-enyl)cyclohexa-3,5-dienone (II). It is proposed that the second Diels–Alder adduct is an intermediate in a reaction which enables an *ortho–ortho* rearrangement of the allyl group in (II) to take place *before* conversion of (II) into (V). This reaction has been observed using pentafluorophenyl [2,3,3-<sup>2</sup>H<sub>3</sub>]prop-2-enyl ether (XII), which on pyrolysis not only gives [3,3aβ,5α-<sup>2</sup>H<sub>3</sub>]-2,5,6,7,7aβ-pentafluoro-3a,4,5,7a-tetrahydroinden-1-one (XV) (9 parts), the product expected from the intermediate 2-([1,1,2-<sup>2</sup>H<sub>3</sub>]prop-2-enyl)cyclohexa-3,5-dienone (XIII) but also [3aβ,4,4-<sup>2</sup>H<sub>3</sub>]-2,5β,6,7,7aβ-pentafluoro-3a,4,5,7a-tetrahydroinden-1-one (XVIII) (10 parts) from 2-([2,3,3-<sup>2</sup>H<sub>3</sub>]prop-2-enyl)-cyclohexa-3,5-dienone (XIX) formed by the prior *ortho–ortho* rearrangement of (XIII).

In a previous paper we described the pyrolysis of pentafluorophenyl prop-2-enyl ether (I) at 365° to give 2,3,4,5,6-pentafluoro-4-(prop-2-enyl)-2,5-cyclohexadienone (III).<sup>1</sup> Our original intention was to devise a simple synthesis of 5,6,7,8-tetrafluorochromen (IV) which could then be oxidised to 6-carboxy-2,3,4,5-tetrafluorophenoxycetic acid,<sup>2</sup> a precursor for the synthesis of derivatives of 4,5,6,7-tetrafluorobenzo[*b*]furan. The scheme envisaged the pyrolytic dehydrofluorination of the initially formed Claisen rearrangement product (II), followed by an electrocyclic ring closure (Scheme 1).

In an attempt to promote dehydrofluorination of the initially formed dienone (II), the ether (I) was distilled *in vacuo* through a quartz tube packed with silica fibre heated to 480°. The major component (33%) of the complex product, separated by chromatography on silica, was shown by elemental analysis and mass spectrometry to be isomeric with the starting material (I), and was assigned the structure (V) on the basis of spectroscopic data taken in conjunction with plausible isomerisation reactions. The i.r. spectrum showed characteristic absorptions at 3100 (vinylic C–H), 2950 (aliphatic C–H),

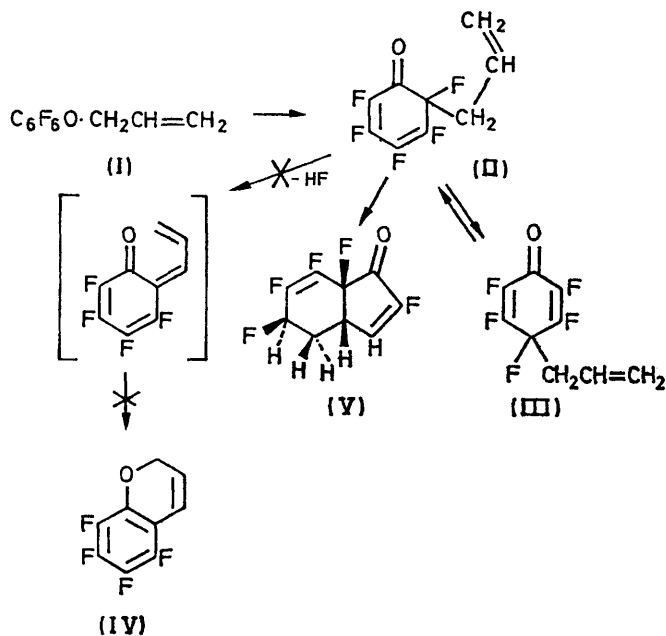
1753 (αβ-unsaturated ketonic >C=O), 1737 (CF=CF), and 1648 cm<sup>-1</sup> which is consistent with CH=CF conjugated with >C=O. The presence of a conjugated ketone was further shown from the u.v. spectra. The <sup>1</sup>H and <sup>19</sup>F n.m.r. spectra of (V), however, clearly showed the profound change which had taken place during the pyrolysis: the presence of >CHF was evident from *J*<sub>gem H,F</sub> 50 Hz. The <sup>1</sup>H n.m.r. spectrum showed in addition, one vinylic proton (τ 2.75; no major coupling), a tertiary C–H (τ 6.45) and two aliphatic hydrogen atoms (centred at τ 7.55). A partial analysis of the n.m.r. data of (V) is shown in the Table. The doublet for F-2 (*J*<sub>2F,3aH</sub> 7 Hz) is noteworthy (see below).

The structure (V) has been substantiated by further chemical reactions. When (V) was heated at 175–185° in a stream of nitrogen, dehydrofluorination occurred and the orange unstable 2,6,7-trifluoroindenone (VI) (half-life *ca.* 2 h at room temperature) (identified by i.r. and mass spectroscopy) was isolated from the complex mixture of products by chromatography on silica. Catalytic hydrogenation of (VI) gave the 2,6,7-trifluoroindan-1-ol (VII) which was partially oxidised by H<sub>2</sub>CrO<sub>4</sub> to 2,6,7-trifluoroindan-1-one (VIII), the further oxidation of which gave 3,4-difluorophthalic acid (IX);

<sup>1</sup> G. M. Brooke, *Tetrahedron Letters*, 1971, **26**, 2377.

<sup>2</sup> G. M. Brooke and B. S. Furniss, *J. Chem. Soc. (C)*, 1967, 869.

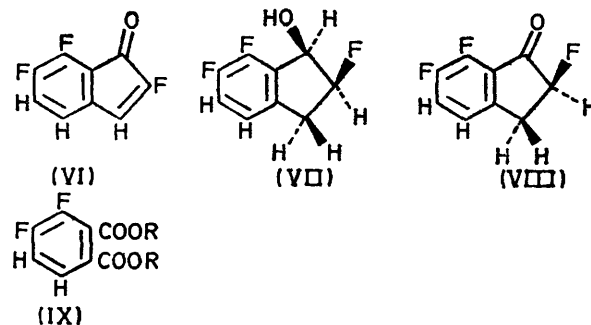
R = H), identified as its dimethyl ester (IX; R = Me). The structure and stereochemistry of (VII) has been



demonstrated unambiguously by  $^{19}\text{F}$  and  $^1\text{H}$  n.m.r. spectroscopy in conjunction with the lanthanide shift reagent  $\text{Eu}(\text{fod})_3$ .<sup>3</sup>

pyrolysis tube, even at  $480^\circ$ , must be responsible for the further decomposition of (V) being of only minor importance in these reactions.

The formation of (V) from both the ether (I) and the 2,5-dienone (III) can be explained by considering a reaction pathway which involves a common intermediate,



the 2,4-dienone (II) which is expected to be formed by reversible, thermally induced, symmetry-allowed [3,3] sigmatropic rearrangements.<sup>4</sup> Although (II) has not been isolated and used in any of the experiments, its conversion into (X), one of the two possible internal Diels-Alder adducts, followed by cleavage of a C-C bond to give the relatively stable diradical (XI) and then hydrogen migration from C-3 to C-5 would give (V) (Scheme 2). (The same overall results could be achieved by postulating an initial heterolytic fission of the same

N.m.r. spectral data <sup>a</sup>

Compound (V)			Mixture of (XV) and (XVIII)		
Atom <sup>b</sup>	Shift <sup>c</sup>	Coupling constants <sup>d</sup>	Atom <sup>b,e</sup>	Shift <sup>c</sup>	Coupling constants <sup>d</sup>
$^{19}\text{F}$					
F-2 (1)	-1474 (-26.1)	$J_{2\text{F},3\text{aH}} 7$ (ca. 5)	F-2 (0.474)	-1462 (-25.9)	0 (ca. 5)
F-5 (1)	+1387 (+24.6)	$J_{5\text{F},6\text{F}} 25$ $J_{5\text{F},4\text{H}} \begin{cases} 15.5 \\ 15.5 \end{cases}$ } (ca. 5)	F-2' (0.526)	-1476 (-26.2)	0 (ca. 5)
F-6 (1)	-1422 (-25.2)	$J_{5\text{F},6\text{F}} 25$ (ca. 14)	F-5' (1)	Overlapping spectra at ca. +1412 (+25.0)	Complex (ca. 5)
F-7 (1)	-562 (-10.0)	$J_{7\text{F},7\text{aF}} 28.5$ (ca. 13)	F-6' (1)	-1420 (-25.2)	$J_{5\text{F},6\text{F}} 25$ (ca. 10)
F-7a (1)	-98 (-1.7)	$J_{7\text{F},7\text{aF}} 28.5$ $J_{7\text{aF},3\text{aH}} 18$ } (ca. 10)	F-7' (1)	-560 (-9.9)	$J_{7\text{F},7\text{aF}} 28.5$ (ca. 12)
$^1\text{H}$			F-7a' (1)	-96 (-1.7)	$J_{7\text{F},7\text{aF}} 28.5$ (ca. 20)
H-3 (1)	2.75	Minor coupling <1.5 (ca. 6)	H-3' (1)	2.77	Minor coupling <1.5 (ca. 5)
H-4 (2)	7.55	Complex multiplet	H-4 (1.8)	7.59	$J_{4\text{H},5\text{F}} 15$ (ca. 5)
H-5 (1)	4.63	$J_{\text{gem F,H}} 51$ (ca. 20)	H-5' (1)	4.65	$J_{\text{gem F,H}} 51$ (ca. 15)
H-3a (1)	6.45	$J_{7\text{aF},3\text{aH}} 18$ (ca. 16)			

<sup>a</sup> Spectra run in  $[\text{D}_6]\text{acetone}$ . <sup>b</sup> Integrated intensities in parentheses. <sup>c</sup> Shifts for  $^{19}\text{F}$  are expressed in both Hz and p.p.m. (in parentheses) upfield (+) or downfield (-) with respect to internal  $\text{C}_6\text{F}_6$  as reference; for  $^1\text{H}$ , shifts are in  $\tau$  values with respect to internal  $\text{Me}_4\text{Si}$  as reference. <sup>d</sup> Coupling constants in Hz; half height linewidths (Hz) in parentheses. <sup>e</sup> Superscript prime refers to the atoms of compound (XVIII).

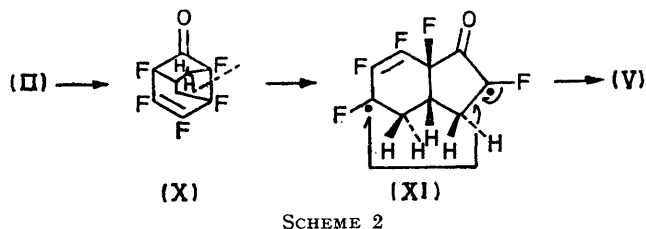
Pyrolysis of the dienone (III) at  $480^\circ$  under the same conditions which were used for the pyrolysis of (I) also gave compound (V) (28%) as the major component in a complex mixture. In both of these high temperature reactions the formation of (V) was accompanied by the presence of small amounts of an orange material, presumably the indenone (VI) formed by dehydrofluorination of (V). The much shorter contact time in the

C-C bond, though this would probably be less economical in terms of energy requirements.) Inspection of molecular models shows that one conformation of the diradical (XI) exists in which a hydrogen at position 3 lies very close to the radical centre at C-5 to permit easy hydrogen

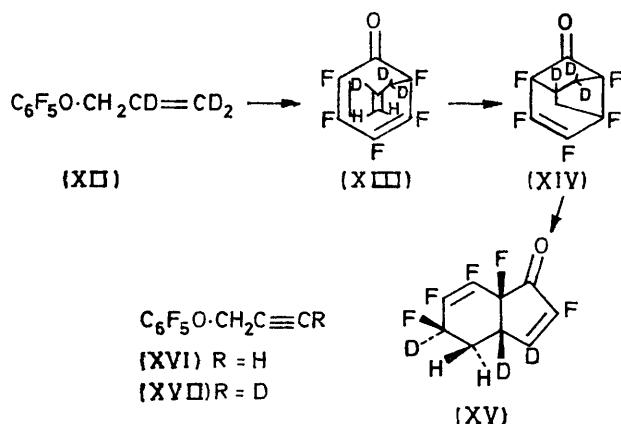
<sup>3</sup> G. M. Brooke and R. S. Matthews, *Tetrahedron Letters*, 1973, 3469.

<sup>4</sup> A. Jefferson and F. Scheinman, *Quart. Rev.*, 1968, 22, 391.

transfer. The alternative possibility of transfer of a hydrogen at position 4 to the radical centre at C-2 to form a 1,3-diene, has a much less favourably disposed geometry and has not been found to take place.



According to this reaction scheme, the hydrogen atoms at positions 3 and 5 in compound (V) are derived from the two terminal vinylic hydrogen atoms in (I) and in order to test this proposition further, pentafluorophenyl [2,3,3-<sup>2</sup>H<sub>3</sub>]prop-2-enyl ether (XII) was synthesised. Hexafluorobenzene reacted with the sodium salt of the propargyl alcohol in tetrahydrofuran to give pentafluorophenyl prop-2-ynyl ether (XVI) which on metallation with *n*-butyl-lithium and treatment with deuterium oxide gave the [3-<sup>2</sup>H]prop-2-ynyl ether (XVII); catalytic partial deuteration of (XVII) gave (XII). It was anticipated that pyrolysis of (XII) would give (XV) *via* the dienone (XIII) and the internal Diels-Alder adduct (XIV).



Pyrolysis of the [2,3,3-<sup>2</sup>H<sub>3</sub>]prop-2-enyl ether (XII) at 480° under conditions identical with those used for (I) did not give exclusively (XV); a mixture of (XV) and the isomer (XVIII) was formed in the ratio (9 : 10), and was identified by spectroscopy. A partial analysis of the n.m.r. data is shown in the Table. The <sup>1</sup>H n.m.r. spectrum showed a doublet at  $\tau$  7.59 ( $J_{4H,5F}$  15 Hz) due to the CH<sub>2</sub> from (XV), but in addition showed absorptions of equal intensity at  $\tau$  2.77 (vinylic C-H; no major coupling) and 4.65 (CHF;  $J_{gem F,H}$  51 Hz) assigned to (XVIII). The absorption at  $\tau$  6.45 (tertiary C-H) found in the spectrum of (V) was conspicuously absent. The relative intensities of the absorptions due to (XV)

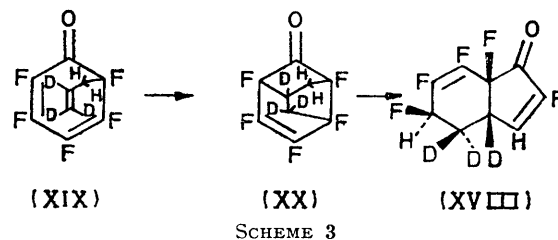
<sup>5</sup> J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, 1967, **89**, 5303; J. A. Berson, *Accounts Chem. Res.*, 1968, **1**, 152.

<sup>6</sup> H. Kwart and N. Johnson, *J. Amer. Chem. Soc.*, 1970, **92**, 6064.

and (XVIII) were consistent with the isomer ratio obtained from the <sup>19</sup>F n.m.r. spectrum. The <sup>19</sup>F n.m.r. spectrum showed that the fluorine atoms at positions 6, 7, and 7a in (XV) and (XVIII) were essentially magnetically identical and unshifted relative to the corresponding absorptions found in (V), while the absorptions at position 5 differed to such an extent as to deny simple analysis. Two absorptions were found in the region expected for 'F-2' and the absence of splitting in either of them confirmed the assignment previously noted for  $J_{2F,3aH}$  7 Hz in (V). The absorption at the lower field (-1476 Hz from C<sub>6</sub>F<sub>6</sub>) was assigned to the fluorine at C-2 in (XVIII) since the magnetic environment would be expected to be very similar to that found for F-2 in (V) (-1474 Hz). The absorption at F-7a given by the mixture of (XV) and (XVIII) was much simpler than the corresponding absorption in (V) and confirmed the assignment made in (V) for  $J_{7aF,3aH}$  18 Hz; molecular models predict the *cis*-configuration for atoms 7a-F and 3a-H. The i.r. spectrum of the product from the pyrolysis of (XII) was also consistent with it being a mixture of (XV) and (XVIII). Absorptions at 2320 (vinylic C-D) and 1630 cm<sup>-1</sup> (CD=CF conjugated with C=O) were due to (XV) while those at 3100 (vinylic C-H) and 1648 cm<sup>-1</sup> {CH=CF conjugated with C=O [cf. 1648 cm<sup>-1</sup> in (V)]} were due to (XVIII).

The conversion of the ether (XII) into (XV) requires the dienone (XIII) and Diels-Alder adduct (XIV) as intermediates, but according to the mechanism postulated above, the formation of (XVIII) requires (XIX) and (XX) as precursors (Scheme 3). A number of possible routes to the *ortho*-dienone (XIX) need to be considered.

(i) *Prior Isomerisation of the Ether (XII)*,  $C_6F_5O-CH_2CD=CD_2 \rightarrow C_6F_5O-CD_2CD=CH_2$  followed by *Claisen Rearrangement*.—While the thermal [1,3] sigmatropic shift of an *alkyl* group with inversion has been observed,<sup>5</sup> the isomerisation  $C_6H_5S-CD_2CH=CH_2 \rightleftharpoons C_6H_5S-CH_2CH=CD_2$  studied by Kwart did not have the characteristics of a sigmatropic rearrangement. Furthermore, a study of the thermal reactions of  $C_6H_5O-CH_2CD=CD_2$  showed that the expected *ortho*-Claisen



rrearrangement product was obtained; no prior isomerisation of the ether had taken place.<sup>6</sup> Consequently, there is no precedent for invoking prior isomerisation of (XII) as a route to (XIX).<sup>7</sup>

(ii) *Direct Formation from (XIII) by a Concerted ortho-ortho Rearrangement*.—A [3,5] thermally induced

<sup>7</sup> T. L. Gilchrist and R. C. Storr, 'Organic Reactions and Orbital Symmetry,' Cambridge University Press, Cambridge, 1972, p. 229.

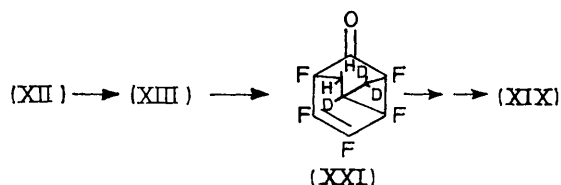
shift would be allowed only as a suprafacial, antarafacial process, and considerations of transition state geometry would preclude this possibility.

(iii) *A [3,5] Sigmatropic Shift of the Allyl Group in the Ether (XII) from Oxygen to the para-Carbon, followed by Cope Rearrangement of the Allyl Group to the ortho-Position.*—This possibility is excluded because the [3,5] shift is forbidden by orbital symmetry consideration<sup>8</sup> [see (ii)].

(iv) *Formation of the Expected 2,5-Dienone by Two Successive [3,3] Shifts followed by Two Successive Acid-catalysed Wagner–Meerwein Rearrangements.*—Allylic migrations in acid-catalysed dienone–dienone rearrangements have been observed by Miller.<sup>9</sup> However, the conditions employed in the experiments described in this paper (high temperature reactions at low vapour pressures) are unlikely to promote this rearrangement even though traces of HF and DF would be present by further decomposition of (XV) and (XVIII).

(v) *Homolysis to Free Phenoxyl (C<sub>6</sub>F<sub>5</sub>O) and Allyl (ĊH<sub>2</sub>CD=CD<sub>2</sub> ↔ CH<sub>2</sub>=CDĊD<sub>2</sub>) Radicals and Recombination.*—The intramolecular nature of the Claisen rearrangement is very well established and although quasi-radical structures for transition states have been suggested by some workers, there is no compelling evidence for this.<sup>10</sup> It is difficult to envisage the formation (XIX) from (XII) by this mechanism.

(vi) *Formation of the Second Possible Diels–Alder Adduct (XXI) from (XIII) followed by a Stepwise Rearrangement.*—There are no problems connected with this mechanism. The analogous reaction starting with



(XIX) instead of (XIII) allows re-formation of (XIII), so that the product ratio (XV) : (XVIII) (9 : 10) could represent the ratio of their precursors, (XIII) : (XIX) in equilibrium at 480°. Schmid has invoked this mechanism to account for the redistribution of radioactivity between the  $\alpha$ - and the  $\gamma$ -carbon atoms of the allyl group in the [ $\gamma$ -<sup>14</sup>C]prop-2-enyl ether of 2,4,6-trimethylphenol.<sup>11</sup>

The attractiveness of this last mechanism becomes even more apparent when it is realised that simple molecular models indicate that the formation of adducts analogous to (XXI) should be much easier than the formation of adducts analogous to (XIV). Consequently, in order to account for the products obtained in the pyrolysis of pentafluorophenyl [2,3,3-<sup>2</sup>H<sub>3</sub>]prop-2-enyl ether (XII), both possible *types* of Diels–Alder

adducts of the intermediate 2,4-dienones must be invoked. One type is involved in the *ortho–ortho* isomerisation reaction [(XIII) ↔ (XIX)], while the other type is involved in the subsequent reactions which lead to the products [(XV) and (XVIII)]. The full description of the chemistry involved in the pyrolysis of pentafluorophenyl prop-2-enyl ether (I) at 480° must therefore include the degenerate *ortho–ortho* rearrangement of the dienone (II), proceeding *via* one internal Diels–Alder adduct, which is then followed by the formation of the product (V) *via* the second internal Diels–Alder adduct (X). While internal Diels–Alder adducts analogous to (XIV) and (XXI) have not yet been isolated from the rearrangement of allyl phenyl ethers, adducts have been obtained from the rearrangement of aryl propargyl ethers.<sup>12</sup> Experiments are now in progress to try to isolate the two adducts which are the proposed intermediates in the higher temperature pyrolysis of (I).

#### EXPERIMENTAL

*Pentafluorophenyl Prop-2-enyl Ether (I).*—A mixture of pentafluorophenol (86.6 g), allyl bromide (100 ml), and anhydrous potassium carbonate (100 g) in dry acetone (300 ml) was heated under reflux for 16 h, filtered and the filtrate distilled *in vacuo*. The main fraction (b.p. ca. 50° at 8 mmHg) was diluted with ether, washed with caustic soda (4N), and the organic phase separated, dried (MgSO<sub>4</sub>), and evaporated. Distillation of the residue *in vacuo* gave *pentafluorophenyl prop-2-enyl ether* (I) (87.9 g), b.p. 59° at 12 mmHg (Found: C, 48.3; H, 2.2. C<sub>9</sub>H<sub>5</sub>F<sub>5</sub>O requires C, 48.2; H, 2.2%).  $\tau$  (neat) 5.28 (d,  $J_{1H,2H}$  6 Hz, CH<sub>2</sub>).

Treatment of hexafluorobenzene in tetrahydrofuran at reflux with a suspension of the sodium salt of allyl alcohol (1 equiv.) in tetrahydrofuran gave (I) in 65% yield.

*Pentafluorophenyl Prop-2-ynyl Ether (XVI).*—Propargyl alcohol (3.5 g) in dry tetrahydrofuran (20 ml) was treated with sodium hydride (1.24 g). The mixture was diluted with further tetrahydrofuran (20 ml) and added over 10 min to hexafluorobenzene (12 g) at reflux temperature to maintain boiling without external heating. Tetrahydrofuran (15 ml) was added and the solution was heated under reflux for 3 min, diluted with ether, and washed with water. The organic phase was dried (MgSO<sub>4</sub>), the solvent evaporated, and the residue distilled *in vacuo* to give the *prop-2-ynyl ether* (XVI) (8.28 g), b.p. 57° at 11 mmHg (Found: C, 48.5; H, 1.4%; M<sup>+</sup>, 222. C<sub>9</sub>H<sub>3</sub>F<sub>5</sub>O requires C, 48.6; H, 1.4%; M, 222),  $\tau$  (neat) 5.14 (2H, d, CH<sub>2</sub>) and 7.45 (1H, t,  $J_{1H,3H}$  2.4 Hz, C≡CH).

*Pentafluorophenyl [3-<sup>2</sup>H]Prop-2-ynyl Ether (XVII).*—The ether (XVI) (15.0 g) in dry tetrahydrofuran (250 ml) was cooled to –70° in an atmosphere of nitrogen, and n-butyllithium in hexane (42 ml; 1.88M) was added over 1.5 h, the temperature being maintained at –70° throughout. The mixture was treated with deuterium oxide (5 ml) in dry tetrahydrofuran (75 ml) at –68 to –72°, warmed to 10°, and dried (MgSO<sub>4</sub>). The mixture was filtered, the drying agent washed with ether, and the solvents evaporated. Distillation of the residue *in vacuo* gave a product (9.71 g), b.p. 61° at 12 mmHg, which contained two components. These were separated by chromatography on

<sup>11</sup> P. Fahrni and H. Schmid, *Helv. Chim. Acta*, 1959, **42**, 1102; H. J. Hansen and H. Schmid, *Chem. in Brit.*, 1969, **5**, 111.

<sup>12</sup> J. Zsindely and H. Schmid, *Helv. Chim. Acta*, 1968, **51**, 1510.

<sup>8</sup> B. Miller in 'Mechanisms of Molecular Rearrangement,' ed. B. S. Thyagarajan, vol. 1, Interscience, New York, 1968, p. 225.

<sup>9</sup> B. Miller, *Chem. Comm.*, 1968, **22**, 1435.

<sup>10</sup> D. L. H. Williams in 'Comprehensive Chemical Kinetics. Reactions of Aromatic Compounds,' vol. 13, eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, p. 467.

silica [petroleum (b.p. 40–80°) as eluant] to give the [3-<sup>2</sup>H]*prop-2-ynyl ether* (XVII) (7.5 g), b.p. 73° at 20 mmHg (Found: *M*<sup>+</sup>, 223. C<sub>9</sub>H<sub>2</sub>DF<sub>3</sub>O requires *M*, 223). The <sup>1</sup>H n.m.r. of (XVII) (neat liquid) showed a singlet at τ 5.14 (CH<sub>2</sub>) and a low intensity triplet at τ 7.45 (C≡CH) due to the presence (<5%) of the non-deuteriated ether (XVI).

*Pentafluorophenyl* [2,3,3-<sup>2</sup>H<sub>3</sub>]*Prop-2-enyl Ether* (XII).—The ether (XVII) (11.57 g) in ethyl acetate (50 ml) was stirred vigorously with 5% Pd–BaSO<sub>4</sub> (1 g) in an atmosphere of deuterium at room temperature and pressure. The reaction was stopped when the deuterium uptake was 1 mol. equiv. The solution was filtered, the solvent evaporated, and the residue distilled *in vacuo* to give the [2,3,3-<sup>2</sup>H<sub>3</sub>]*prop-2-enyl ether* (XII) (9.63 g), b.p. 53° at 9 mmHg (Found: *M*<sup>+</sup>, 227. C<sub>9</sub>H<sub>2</sub>D<sub>3</sub>F<sub>3</sub>O requires *M*, 227), τ (neat) 5.33 (s, CH<sub>2</sub>).

*Pyrolysis of Pentafluorophenyl Prop-2-enyl Ether* (I).—The ether (I) (12.2 g) was distilled over 55 min from a vessel at 65° through a silica tube (20 mm long × 1.5 mm diameter) packed with silica fibre and heated to 480°, into a trap cooled with liquid air connected to a high vacuum system (0.05–0.1 mmHg). The major component of the complex product was separated by chromatography on silica (chloroform as eluant) to give 2,5β,6,7,7aβ-*pentafluoro-3aβ,4,5,7a-tetrahydroinden-1-one* (V) (4.02 g), m.p. 84.5–86.5° [from benzene–petroleum (b.p. 60–80°)] (Found: C, 48.4; H, 2.3; F, 42.8%; *M*<sup>+</sup>, 224. C<sub>9</sub>H<sub>3</sub>F<sub>5</sub>O requires C, 48.2; H, 2.2; F, 42.4%; *M*, 224), ν<sub>max</sub> 3100 (vinylic C–H), 2950 (aliphatic C–H), 1753 (C=O conjugated with C=C), 1737 (CF=CF), and 1648 cm<sup>-1</sup> (CH=CF conjugated with C=O), λ<sub>max</sub> (ethanol) 237 (ε 5040) and 334 nm (ε 147).

*Pyrolysis of 2,3,4,5,6-Pentafluoro-4-(prop-2-enyl)cyclohexa-2,5-dienone* (III).—The dienone (III) (0.575 g) was pyrolysed as in the previous experiment to give compound (V) (0.163 g), identified by i.r. spectroscopy.

*Pyrolysis of Pentafluorophenyl* [2,3,3-<sup>2</sup>H<sub>3</sub>]*Prop-2-enyl Ether* (XII).—The ether (XII) (8.68 g) was pyrolysed as in the previous experiment to give a mixture of [3,3aβ,5α-<sup>2</sup>H<sub>3</sub>]-2,5,6,7,7aβ-*pentafluoro-* (XV) and [3aβ,4,4-<sup>2</sup>H<sub>3</sub>]-2,5β,6,7,7aβ-*pentafluoro-3a,4,5,7a-tetrahydroinden-1-one* (XVIII) (2.45 g), m.p. 85–86° (Found: *M*<sup>+</sup>, 227. C<sub>9</sub>H<sub>2</sub>D<sub>3</sub>F<sub>5</sub>O requires *M*, 227), ν<sub>max</sub> 3100 (vinylic C–H), ca. 2950 (aliphatic C–H), 2320 (vinylic C–D), ca. 2200 (aliphatic C–D), 1751 (C=O conjugated with C=C), 1736 (CF=CF), 1648 (CH=CF conjugated with C=O), and 1630 cm<sup>-1</sup> (CD=CF conjugated with C=O), λ<sub>max</sub> (ethanol) 234 (ε 5770) and 335 nm (ε 138).

*Action of Heat on Compound* (V).—Compound (V) (10.3 g) (ten separate experiments) was heated in a U tube at 175–185° through which a rapid stream of nitrogen was passed, and the volatile components were collected in a trap cooled with liquid air. The yellow-orange product was dissolved in chloroform, washed with water, dried (MgSO<sub>4</sub>), and reduced to small bulk by evaporation *in vacuo* at room temperature. The coloured component in the complex mixture was separated as the fastest moving component by chromatography on silica (chloroform as eluant), and evaporation of the solvent *in vacuo* at room temperature and sublimation at 40° and 0.05 mmHg gave crude 2,6,7-trifluoroindenone (VI) (2.04 g) m.p. 72–85° (Found: *M*<sup>+</sup>, 184. Calc. for C<sub>9</sub>H<sub>3</sub>F<sub>3</sub>O: *M*, 184), ν<sub>max</sub> 3060 (vinylic C–H),

1740 (C=O conjugated with C=C), 1645 (CH=CF conjugated with C=O), and 1500 cm<sup>-1</sup> (fluorine-containing benzene ring).

2,6,7-*Trifluoroinden-1-ol* (VII).—The indenone (VI) (2.04 g) was dissolved in ethyl acetate and exhaustively hydrogenated over Pd–C (20 mg) at room temperature and pressure [uptake: ca. 2 mole H<sub>2</sub> per mole (VI)]. The solution was filtered, the solvent evaporated, and the residue crystallised from benzene–petroleum to give 2,6,7-*trifluoroinden-1-ol* (VII) (1.27 g), m.p. 83.0–83.5° (Found: C, 57.6; H, 3.6%; *M*<sup>+</sup>, 188. C<sub>9</sub>H<sub>3</sub>F<sub>3</sub>O requires C, 57.4; H, 3.7%; *M*, 188). The <sup>19</sup>F n.m.r. spectrum of (VII) (CCl<sub>4</sub>) showed δ 21.5 (F-6), 17.6 (F-7) downfield and 36.9 p.p.m. (F-2) upfield from internal C<sub>6</sub>F<sub>6</sub> (ratio 1 : 1 : 1) (*J*<sub>gem,2F,2H</sub> 53, *J*<sub>2F,1H</sub> 24, *J*<sub>2F,3H</sub> 24; 12.5 Hz). The <sup>1</sup>H n.m.r. spectrum (CCl<sub>4</sub>) showed τ 3.17 (ArH) and 4.90 (CHF).

2,6,7-*Trifluoroinden-1-one* (VIII).—The inden-1-ol (VII) (1.13 g), chromium trioxide (4.5 g), sulphuric acid (4 ml; *d* 1.84), and water (45 ml) were heated under reflux for 10 min, the mixture was extracted with ether, and the dried (MgSO<sub>4</sub>) extracts evaporated. The crude residue (1.12 g) was crystallised from benzene–petroleum (b.p. 60–80°) to give 2,6,7-*trifluoroinden-1-one* (VIII) (0.54 g), m.p. 100–101° (Found: C, 57.9; H, 2.6%; *M*<sup>+</sup>, 186. C<sub>9</sub>H<sub>3</sub>F<sub>3</sub>O requires C, 58.1; H, 2.7%; *M*, 186). The <sup>19</sup>F n.m.r. spectrum of (VIII) (CDCl<sub>3</sub>) showed δ ca. 23.6 downfield and 29.5 p.p.m. upfield from internal C<sub>6</sub>F<sub>6</sub> (ratio 2 : 1) (*J*<sub>gem,2F,2H</sub> 50.5, *J*<sub>2F,3H</sub> 22.5; 9.5 Hz).

*Dimethyl 3,4-Difluorophthalate* (IX; R = Me).—The inden-1-one (VIII) (1.06 g), chromium trioxide (6.0 g), sulphuric acid (6.0 ml; *d* 1.84), and water (60 ml) were heated under reflux for 2 h after which the mixture was distilled in steam to remove unchanged ketone (VIII). The aqueous solution was extracted with ether, the extracts dried (MgSO<sub>4</sub>), and evaporated to give the crude product (0.72 g). This material was leached with boiling benzene, and the insoluble fraction (IX; R = H) (0.45 g) was treated with excess of diazomethane in ether. The product (0.52 g) was distilled *in vacuo* (b.p. 76–88° at 0.01 mmHg) and the distillate (0.40 g) was crystallised from benzene–petroleum (b.p. 60–80°) to give *dimethyl 3,4-difluorophthalate* (IX; R = Me) (0.20 g), m.p. 55–56.5° (Found: C, 52.0; H, 3.7%; *M*<sup>+</sup>, 230. C<sub>10</sub>H<sub>8</sub>F<sub>2</sub>O<sub>4</sub> requires C, 52.3; H, 3.5%; *M*, 230). The <sup>19</sup>F n.m.r. spectrum of (IX; R = Me) (CDCl<sub>3</sub>) showed δ 22.5 (F-3) and 33.1 (F-4) p.p.m. downfield from internal C<sub>6</sub>F<sub>6</sub> (ratio 1 : 1) (*J*<sub>F,F</sub> 20.5 Hz). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed τ 2.20 (H-6) and 2.66 (H-5) (AB, ArH) (*J*<sub>5,6</sub> 9, *J*<sub>3F,5H</sub> 4.5, *J*<sub>3F,6H</sub> 1.5, *J*<sub>4F,5H</sub> 9, *J*<sub>4F,6H</sub> 7.5 Hz), and 6.05 and 6.14 (2 × Me) (ratio 1 : 1 : 3 : 3).

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