PYROLYSES OF PENTAFLUOROPHENYL 2-METHYLPROP-2-ENYL ETHER.
REACTIONS PROCEEDING VIA INTERNAL DIELS-ALDER REACTIONS, AND
THE CONTRASTING THERMOLYSIS OF PENTAFLUOROPHENYL 2-METHYLBUT-
3-EN-2-YL ETHER

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SUMMARY

The pyrolysis of pentafluorophenyl 2-methylprop-2-enyl
ether (XIII) at 310° gave 4-(2-methylprop-2-enyl)-2,3,4,5,6-
pentafluoro-2,5-cyclohexadienone (XVI) (46%), while at 410° a
mixture of 1-fluorovinyl 2,3,4-trifluoro-5-methylphenyl
ketone (XVIII) (30%) and 2,5β,6,7,7aβ-pentafluoro-3aβ-methyl-
3aβ,4,5,7a-tetrahydroinden-1-one (XXI) (22%) was formed from
the possible internal Diels-Alder adducts (XVII) and (XX)
respectively (Scheme 6). Pentafluorophenyl 2-methylbut-3-en-
2-yl ether (XIV) decomposed under mild conditions (70°C) to
give pentafluorophenyl 3-methylbut-2-en-1-yl ether (XXII),
pentafluorophenol and 2-methyl-1,3-butadiene possibly via an
ion pair intermediate (Scheme 7).

INTRODUCTION

The vapour phase pyrolysis of pentafluorophenyl prop-2-
enyl ether (I) under different conditions has provided products
which are due specifically to presence of fluorine in the
starting material.

For example, at 365°, 2,3,4,5,6-pentafluorophenyl-4-
(prop-2-enyl)-2,5-cyclohexadienone (III) was isolated in 32%
yield via the Claisen rearrangement to (II) followed by a Cope

rearrangement [1] (Scheme 1), which contrasts with only
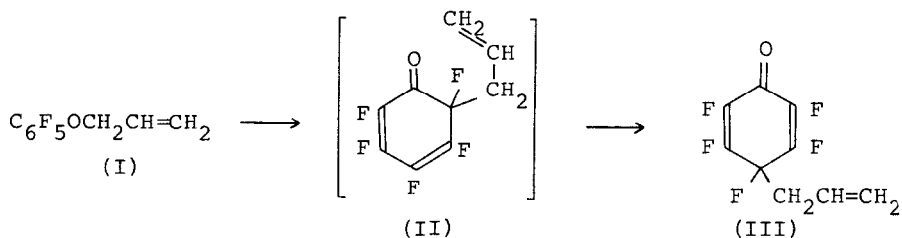
Scheme 1

1.5% of the 2,5-cyclohexadienone (and 0.5% 2,4-cyclohexa-
dienone) present in equilibrium with 2,4,6-trimethylphenyl
prop-2-enyl ether at 180-200° [2]. While the experimental
conditions are different, the relatively high yield of (III)
is evidence of its appreciable thermodynamic stability
compared with the parent ether, and is ascribed in part to
the high stability of the saturated C-F bond.

Furthermore, under vigorous conditions (440°) the ether
(I) was converted into a mixture of 2,3,4-trifluorophenyl 1-
fluorovinyl ketone (V) [3] and 2,5β,6,7,7aβ-pentafluoro-
3aβ,4,5,7a-tetrahydroinden-1-one (VII) [4], their formation
being rationalised in terms of the decomposition of the two
possible intermediate internal Diels-Alder adducts (IV) and
(VI) respectively (Scheme 2). Adducts of the type (IV) had
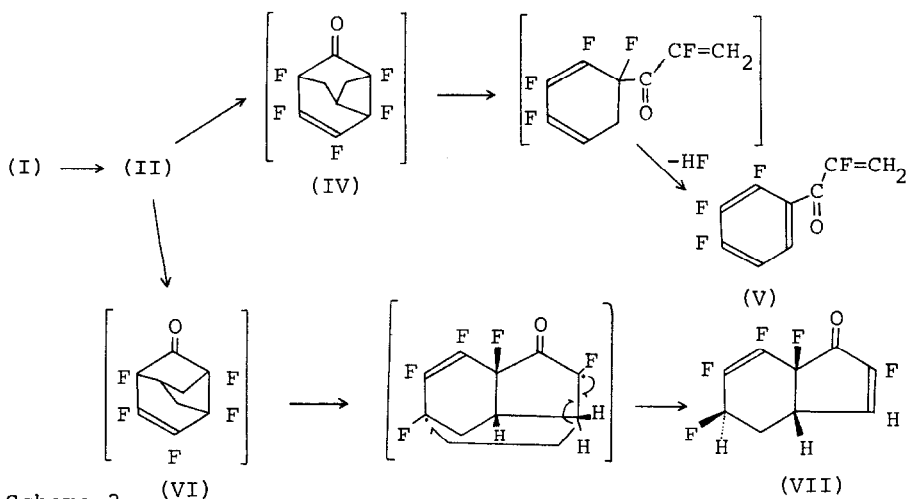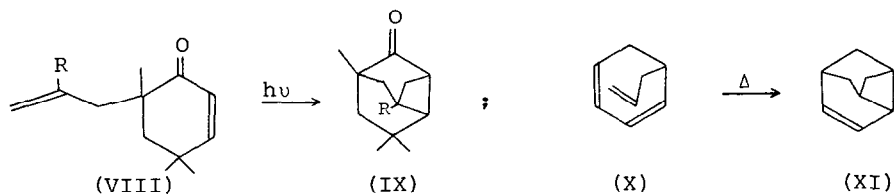

Scheme 2

previously been invoked as intermediates in the equilibration of radioactivity between the 1- and 3-carbon atoms of the prop-2-enyl group during the thermolysis of 2,4,6-trimethyl-phenyl[3-^{14}C]-prop-2-enyl ether [5] (Scheme 3), and indeed
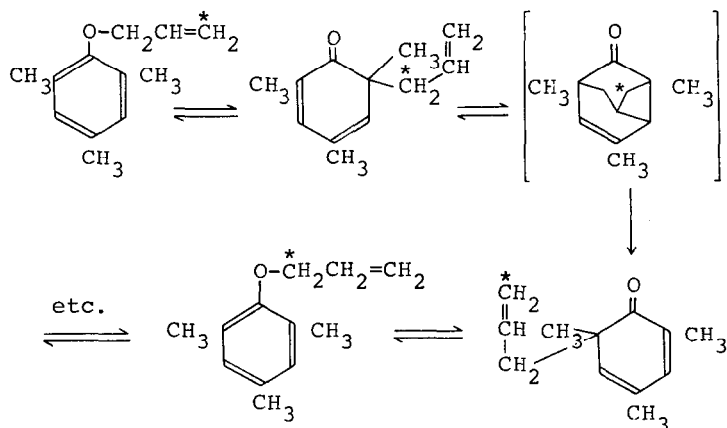
Scheme 3

the operation of this mechanism was necessary to account for the formation of all the products obtained from the pyrolysis of pentafluorophenyl(2,3,3-^{2}H$_3$)-prop-2-enyl ether [4].

The ring system represented by (IV) is a rare example of the [3.3.1.0^{2,7}]tricyclononane skeleton, and only two syntheses of this system have been described in the literature: (i) compound (IX) is one of the products formed from the photochemical reaction of (VIII) [6], and (ii) compound (XI) is produced from (X) by a Diels-Alder reaction [7] (Scheme 4).

(VIII)   (IX)   (X)   (XI)

Scheme 4

In this latter reaction, it is significant that <u>none</u> of the
adduct (XII) is formed by the alternative mode of cycloaddition
(Scheme 5), and while molecular models indicate that this would

(X)   (XII)

Scheme 5

be an energetically unfavourable process, nevertheless the
formation of the inden-1-one (VII) <u>was</u> rationalised on the
intermediacy of the Diels-Alder adduct (VI) of which (XII) is
the prototype [4]. Presumably the high reactivity known to

dienophile [6], and the stabilising influence of aliphatic C-F
bonds must be responsible for this alternative reaction path-
way, the first recorded example of this mode of cycloaddition.
Both types of internal Diels-Alder adducts are formed in the
thermolyses of cycloheptatrienyl prop-2-enyl ether [9] and
3,5,7-trimethyltropone 2-(prop-2-enyl ether) [10], where the
larger rings formed are less strained.

    In this paper we report the vapour phase pyrolysis of
pentafluorophenyl 2-methylprop-2-enyl ether (XIII) and the
liquid phase thermolysis of pentafluorophenyl 2-methylbut-3-en-
2-yl ether (XIV).

RESULTS AND DISCUSSION

    The ether (XIII) was prepared from pentafluorophenol and
2-methylprop-2-en-1-yl chloride and compound (XIV) from the
sodium salt of 2-methylbut-3-en-2-ol and hexafluorobenzene.

    Distillation of the ether (XIII) in vacuo through a quartz
tube packed with silica fibre, at 310° gave a complex product
containing unchanged starting material and 4-(2-methylprop-2-
enyl)-2,3,4,5,6-pentafluoro-2,5-cyclohexadienone (45% conversion)
(XVI), which was identified by spectroscopic methods.

Pyrolysis of the ether (XIII) at 410° also gave a complex product which was separated by a combination of preparative t.l.c. and fractional distillation into 1-fluorovinyl 2,3,4-trifluoro-5-methylphenyl ketone (XVIII) (30%) and 2,5β,6,7,7aβ-pentafluoro-3aβ-methyl-3aβ,4,5,7a-tetrahydroinden-1-one (XXI) (22%). Compound (XVIII) was more stable than the related ketone (V) prepared previously [3], and gave satisfactory analytical data. The structures of (XVIII) and its oxidation product 2,3,4-trifluoro-5-methylbenzoic acid (XIX) were determined by spectroscopic methods. Similarly the inden-1-one (XXI) had spectroscopic properties entirely consistent with the replacement of hydrogen by a methyl group at the 3aβ position in (VII). The products from these experiments are clearly analogous to those obtained from pentafluorophenyl prop-2-enyl ether (I) and indicate the formation and de-composition of a further pair of internal Diels-Alder adducts (XVII) and (XX) (Scheme 6).
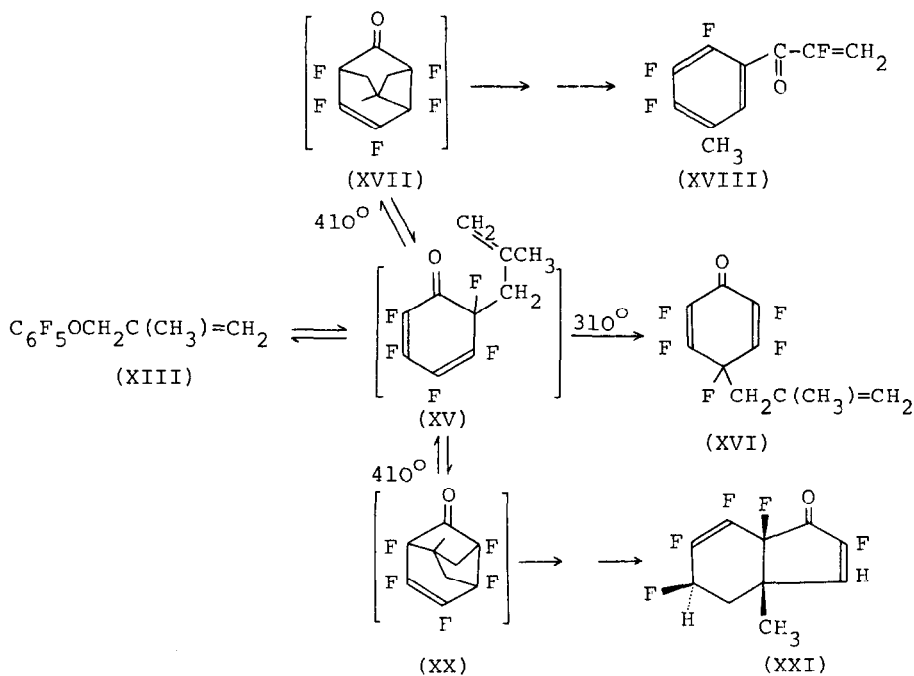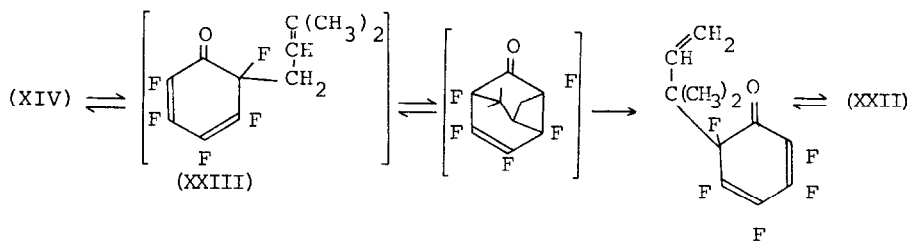

Scheme 6

Pentafluorophenyl 2-methylbut-3-en-2-yl ether (XIV) could never be obtained sufficiently pure to give satisfactory analytical data, though after allowing for the presence of minor impurities, its spectroscopic properties were consistent with its structure. During a careful fractionational distillation of (XIV) in vacuo with an external temperature of $70°$, a volatile gas was evolved and was identified by mass spectroscopy as the dimer of 2-methyl-1,3-butadiene. Pentafluorophenol was also obtained and the higher boiling residue was separated by g.l.c. into unchanged starting material and a new stable product, pentafluorophenyl 3-methylbut-2-en-1-yl ether (XXII), which was prepared independently from the sodium salt of 3-methylbut-2-en-1-ol and hexafluorobenzene. When the ethers (XIV) and (XXII) were heated separately in boiling toluene for 3 days and the mixtures analysed by analytical g.l.c., the only ether identified from (XIV) was (XXII) whereas (XXII) was entirely unchanged under these conditions (Scheme 7).

$$C_6F_5OC(CH_3)_2CH=CH_2 \longrightarrow C_6F_5OH + [CH_2=C(CH_3)CH=CH_2)$$

(XIV)

$$+ \quad C_6F_5OCH_2CH=C(CH_3)_2$$
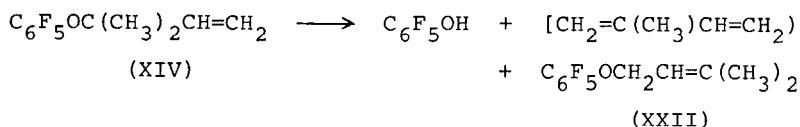
(XXII)

Scheme 7

The formation of (XXII) from (XIV) could be explained in terms of a Claisen rearrangement, followed by an internal Diels-Alder reaction and cleavage of the adduct to give the ortho-ortho rearranged 2,4-dienone which would then re-equilibrate to the aryl ether (XXII) (Scheme 8).

Scheme 8

However, two matters in particular render this explanation unlikely: (i) the absence of the 2,5-dienone compound from the Cope rearrangement of (XXIII); and (ii) the extremely mild conditions under which (XXII) is formed. [In a separate experiment using pentafluorophenyl (2,3,3-^{2}H$_3$)prop-2-enyl ether at 142° for 11.7 days, only 7% isomeric penta-fluorophenyl (1,1,2-^{2}H$_3$)prop-2-enyl ether was formed.]

A recent paper by Whiting [11] suggests an alternative rationalisation of our results. The acetolysis of 2,4-dinitro-phenyl 2-methylbut-3-en-2-yl ether followed first-order kinetics and among the products was the primary 3-methyl-2-buten-1-yl ether (14%). A transition state (XXIV) was proposed.

(XXIV)
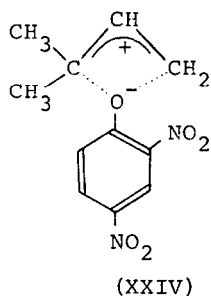
Although the conditions in our reaction are not obviously ionising, the pentafluorophenate group is expected to be at least as good a leaving group as the 2,4-dinitrophenate group and the intermediacy of an ion pair would explain not only the formation of the rearranged ether (XXII) but also the formation of pentafluorophenol and 2-methyl-1,3-butadiene by proton abstraction from the cation moiety by C$_6$F$_5$O$^-$; (2,4-dinitro-phenyl 2-methylbut-3-en-2-yl ether remains stable for some weeks but then rapidly decomposed to the phenol and 2-methyl-1,3-butadiene). However at the present time, we are not able to exclude the possibility of a radical mechanism.

EXPERIMENTAL

Pentafluorophenyl 2-methylprop-2-enyl ether (XIII).

A mixture of pentafluorophenol (50 g), 2-methylprop-2-en-1-yl chloride (37 g), and anhydrous potassium carbonate (50 g) in dry acetone (150 mls) was treated under reflux for 168 h and filtered through anhydrous $MgSO_4$. The filtrate was distilled in vacuo to give the pentafluorophenyl 2-methylprop-2-enyl ether nc (XIII) (51.2 g) b.p. 76° at 14 mm Hg. (Found: C, 50.1; H, 3.1%; M^+, 238. $C_{10}H_7F_5O$ requires C, 50.4; H, 2.9%; M, 238). The ^{19}F n.m.r. spectrum [$(CD_3)_2CO$] showed signals at 159.7 and 167.8 p.p.m. upfield from external $CFCl_3$ in the ratio of 2:3 respectively. The ^1H n.m.r. spectrum [$(CD_3)_2CO$] showed τ 4.98 (H_{syn} + H_{anti}), 5.45 (CH_2), 8.20 (CH_3).

Flow pyrolysis of pentafluorophenyl 2-methylprop-2-enyl ether (XIII) at 310°.

The ether (XIII) (3.0 g) was distilled over 6 h from a vessel at 75° through a silica tube (20 cm x 1.5 cm diam.) packed with silica fibre and heated to 310°, into a trap cooled with liquid air connected to a high vacuum system (0.05 - 0.1 mm Hg). Two components were separated from the complex product by preparative t.l.c. on Kiesel-gel GF_{254} (carbon tetrachloride as eluant). The faster moving component was the ether (XIII) (1.9 g). Sublimation of the slower moving component at 40° and 0.05 mm Hg, and recrystallisation from petroleum (b.p. 30 - 40°) gave 4-[2-methyl-prop-2-enyl]-2,3,4,-5,6-pentafluoro-2,5-cyclohexadienone nc (XVI) (0.5 g) m.p. 32.5 - 32.8° (Found: C, 50.7; H, 2.5%; M^+, 238. $C_{10}H_7F_5O$ requires C, 50.4, H, 2.9%; M, 238). The ^{19}F n.m.r. spectrum [$(CD_3)_2CO$] showed signals at 137.6 (F-3 and F-5), 157.4 (F-2 and F-6) and 159.3 (F-4) p.p.m. upfield from external $CFCl_3$ [$J_{(F-4,F-3)}$ 31.0; $J_{(F-4,F-5)}$ 31.0; $J_{(F-4,CH_2)}$ 11.0 Hz]. The ^1H n.m.r. spectrum [$(CD_3)_2CO$] showed signals at τ, 5.02 (H_{anti}), 5.14 (H_{syn}), 6.93 (CH_2) and 8.35 (CH_3) [$J_{(CH_2,F-4)}$ 11 Hz].

Flow pyrolysis of pentafluorophenyl 2-methyl-prop-2-enyl ether (XIII) at 420°.

The ether (4.8 g) was distilled over 8 h from a vessel at 75° through the packed silica tube as before and heated to 420°, into a trap cooled with liquid air connected to a high vacuum system (0.05 - 0.1 mm Hg). A yellow oil, separated from the complex product by preparative t.l.c. on Kiesel-gel GF_{254} (carbon tetrachloride as eluant), was distilled in vacuo to give 1-fluorovinyl 2,3,4-trifluoro-5-methyl-phenyl ketone nc (XVIII) (1.3 g), b.p. 33° at 0.001 mm Hg (Found: C, 55.3; H, 3.0%; M^+, 218; $C_{10}H_6F_4O$ requires C, 55.1; H, 2.8%; M, 218). The ^{19}F n.m.r. spectrum $[(CD_3)_2CO]$ showed signals at 116.5 (vinylic F), 132.8 (F-4), 139.6 (F-2) and 162.1 (F-3) p.p.m. upfield from external $CFCl_3$. $[J_{(vinylic\ F,\ anti-H)}$ 45.0, $J_{(vinylic\ F,\ syn-H)}$ 13.0, $J_{(vinylic\ F,\ F-2)}$ 13.0, $J_{(F-2,\ F-3)}$ 19.0, $J_{(F-2,\ H-6)}$ 7.0, $J_{(F-3,\ H-6)}$ 2.5, $J_{(F-4,\ H-6)}$ 7.0, $J_{(F-3,\ F-4)}$ 19.0 Hz.]. The ^1H n.m.r. $[(CD_3)_2CO]$ showed τ, 2.84 (H), 4.54$_{(syn-H)}$, 4.57$_{(anti-H)}$, and 7.84 (CH_3); υ_{max} 1690 cm^{-1} (C=O).

The vessel containing the material (3.2 g) remaining after the ketone (XVIII) had been separated, was connected to a trap cooled with liquid air, and the system evacuated (0.05 - 0.1 mm Hg). The volatile material which collected in the trap was distilled in vacuo to give pentafluorophenol (0.2 g) (b.p. 41 - 42°, 4 mm) identified by i.r. spectroscopy. The involatile residue (2.9 g) remaining was separated by chromatography on silica (40 cm x 3.5 cm diam) (chloroform as eluant) to give 2,5β,6,7,7aβ-pentafluoro-3aβ-methyl-3aβ,4,5,7a-tetrahydroinden-1-one nc (XXI) (1.07 g), m.p. 77-78° [from toluene-petroleum/b.p. 80-100°)]. (Found: C, 50.2; H, 3.2%; M^+, 238. $C_{10}H_7F_5O$ requires C, 50.4; H, 3.0%; M, 238). The ^{19}F n.m.r. spectrum $[(CD_3)_2CO]$ showed signals at 139.7 (F-2), 143.4 (F-6), 153.8 (F-7), 177.5 (F-7a) and 193.4 (F-5) p.p.m. upfield from external $CFCl_3$. $[J_{(F-5,\ H-5)}$ 52.0, $J_{(F-5,\ F-6)}$ 24.0, $J_{(F-7,\ F-7a)}$ 29.0, $J_{(F-7a,\ CH_3)}$ 6.0 Hz]. The ^1H n.m.r. $[(CD_3)_2CO]$ showed τ 2.55 (H-3), 4.57 (H-5a), 7.12 - 7.85

(complex multiplet) and 8.45 (CH_3) [$J_{(H-5, F-5)}$ 52.0, $J_{(CH_3, F-7a)}$ 6.0 Hz]; ν_{max} 3080 (vinylic C-H), 2950 (aliphatic C-H), 1759 (C=O conjugated with C=C), 1739 (CF=CF) and 1652 cm^{-1} (CH=CF conjugated with C=O).

2,3,4-Trifluoro-5-methylbenzoic acid (XIX).

The crude vinyl ketone (XVIII) (1.3 g) was heated under

extracts were evaporated. Sublimation of the residue at 130 and 0.05 mm Hg and recrystallisation from toluene-petroleum (b.p. 80-110°) gave 2,3,4-trifluoro-5-methylbenzoic acid nc (XIX) (0.29 g) m.p. 135-136° (Found: C, 50.2; H, 2.8%; M^+ 190. $C_8H_5F_3O_2$ requires C, 50.5; H, 2.6%; M, 190). The ^{19}F n.m.r. spectrum [$(CD_3)_2CO$] showed signals at 132.4 (F-4), 136.2 (F-2), 162.6 (F-3) upfield from external $CFCl_3$. [$J_{(F-2,F-3)}$ 19.0, $J_{(F-2,F-4)}$ 12.0, $J_{(F-3,F-4)}$ 19.0, $J_{(F-3,H-6)}$ 3.0, $J_{(F-2,H-6)}$ 8.0, $J_{(F-4,H-6)}$ 8.0, $J_{(F-4,CH_3)}$ 2.0 Hz]. The ^1H n.m.r. spectrum [$(CD_3)_2CO$] showed τ2.45 (H-6) and 7.83 (CH_3) (external Me_4Si standard); ν_{max} 1700 cm^{-1} (C=O).

Pentafluorophenyl 2-methylbut-3-en-2-yl ether (XIV).

2-Methylbut-3-en-2-ol (4 ml) in dry tetrahydrofuran (30 ml) was treated with sodium hydride (1.6 g). Hexafluorobenzene (12.7 g) in dry tetrahydrofuran (20 ml) was added to the mixture over 20 min. The solution was heated under reflux for 3 min., diluted with ether, and washed with water. The organic phase was dried ($MgSO_4$), the solvent evaporated and the residue distilled in vacuo to give pentafluorophenyl 2-methylbut-3-en-2-yl ether (XIV) (8.48 g), b.p. 82 - 83° at 11 mm Hg. The ^{19}F n.m.r. spectrum (neat) showed signals at 153.4 (F_{ortho}), 165.7(F_{para}) and 167.8(F_{meta}) p.p.m. upfield from external $CFCl_3$. [$J(F_{ortho} - F_{meta})$ 20.0, $J(F_{meta} - F_{para})$ 20.0, $J(F_{ortho} - F_{para})$ 3.0 Hz]. The ^1H n.m.r. spectrum showed τ 3.80 (H-2), 4.73 (H-3$_{anti}$), 4.80 (H-3$_{syn}$) and 8.43 (2 x CH_3).

$[J_{(H-2,H-3_{anti})}$ 18.0, $J_{(H-2,H-3_{syn})}$ 12.0, $J_{(H-3_{anti},H-3_{syn})}$ 3.0 Hz].

Pentafluorophenyl 3-methylbut-2-en-1-yl ether (XXII).

3-Methylbut-2-en-1-ol (0.5 g) in dry tetrahydrofuran (30 ml) was treated with sodium hydride (1.6 g). Hexafluoro-benzene (10.2 g) in dry tetrahydrofuran (50 ml) was added to the mixture over 30 min. The solution was heated under reflux for 3 min., diluted with ether, and washed with water. The organic layer was dried ($MgSO_4$), the solvent evaporated and the residue distilled in vacuo to give pentafluorophenyl 3-methyl-but-2-en-1-yl ether nc (XXII) (5.9 g), b.p. 81-82° at 8 mm Hg. (Found: C, 52.2; H, 3.8%; M^+, 252. $C_{11}H_9F_5O$ requires C, 52.4; H, 3.6%; M, 252). The ^{19}F n.m.r. spectrum (neat liquid) showed signals at 158.4 and 167.0 p.p.m. upfield from external $CFCl_3$ in the ratio of 2:3 respectively. The ^1H n.m.r. spectrum (neat) showed τ 4.72 (H-2), 5.48 (CH_2), 8.43 (CH_3) and 8.48 (CH_3). $[J_{(H-2,CH_2)}$ 7.5 Hz].

Reactions of pentafluorophenyl 2-methylbut-3-en-2-yl ether (XIV)

(a) The ether (XIV) (2.5 g) was heated under reflux, 70° at reduced pressure (8 mm Hg), for 8 hr. A gas which evolved was collected in a trap surrounded by liquid air and was shown to be 2-methyl-1,3-butadiene [mass spect. 132; dimer of C_5H_8 requires 132]. The complex mixture was distilled in vacuo to give pentafluorophenol (0.5 g), b.p. 41° at 7 mm Hg. The higher binding residue was separated using preparative g.l.c. (silicone gum rubber at 140°) into two components: the ether (XIV) (1.1 g) and pentafluorophenyl 3-methylbut-2-en-1-yl (XXII) (0.5 g). [It appears that under the conditions for g.l.c. separation, (XIV) is not significantly isomerised to (XXII)].

(b) The ether (XIV) (0.1 g) in toluene (0.5 mls) was treated under reflux (110°) for 3 days to give pentafluoro-phenyl 3-methylbut-2-en-1-yl ether (XXII) as the exclusive

volatile ether product. When pentafluorophenyl 3-methylbut-
2-en-1-yl (XXII) ether was subjected to the conditions above,
g.l.c. analysis showed that it remained unchanged.

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