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THE PREPARATION AND REACTIONS OF 1,3,4,5,6,7,8-HEPTAFLUORO-2-NAPHTHYL PROP-2-ENYL ETHER: FORMATION OF 1,3,4,5,6,7,8-HEPTAFLUORO-1-(PROP-2-ENYL)NAPHTHALEN-2-ONE AND THE PHOTOLYSIS AND PYROLYSIS OF THIS KETONE [1].

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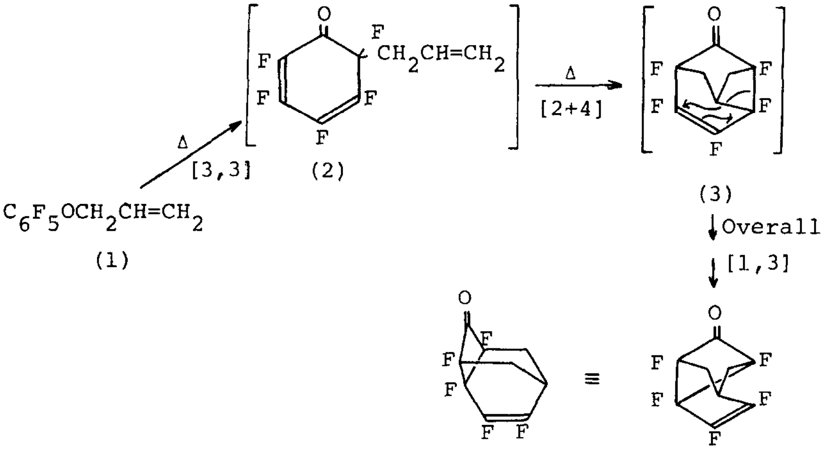
SUMMARY

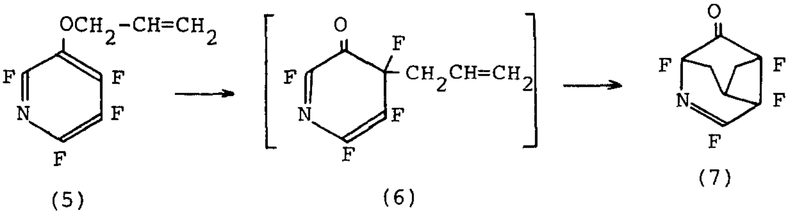
1,3,4,5,6,7,8-Heptafluoro-2-naphthyl prop-2-enyl ether (8) was isomerised in boiling xylene to 1,3,4,5,6,7,8-heptafluoro-1-(prop-2-enyl)naphthalen-2-one (9). Photolysis of (9) gave 2,5,7-trifluoro-3,4-(tetrafluorobenzo)tricyclo[3.3.1.0^{2,7}]non-3-en-6-one (11) (by a [2 + 2] addition) and 1,2,7-trifluoro-3,4-(tetrafluorobenzo)tricyclo[3.3.1.0^{2,7}]non-3-en-8-one (12) (via an initial [3,5] photochemically-allowed sigmatropic shift). Pyrolysis of (9) at 455° also gave (11), while at 490°, both (9) and (11) gave 1-fluorovinyl 4,5,6,7,8-pentafluoro-1-naphthyl ketone (19).

INTRODUCTION

Thermally induced reactions of polyfluoro-aryl and -heteroaryl prop-2-enyl ethers have been shown to give a variety of products which are all derived from an initial [3,3] sigmatropic shift (Claisen Rearrangement). For example pentafluorophenyl prop-2-enyl ether (1) at 137-141° for 13 days gave (4) via the proposed internal Diels-Alder adduct (3) [2] (Scheme 1), while with the tetrafluoro-3-pyridyl compound (5), the actual Diels-Alder adduct (7) was the product [3] (Scheme 2). In none of the cases previously studied has the intermediate 2,4-dienone [e.g. (2) and (6)] been isolated, though 2,3,4,5,6-pentafluoro-4-



Scheme 1

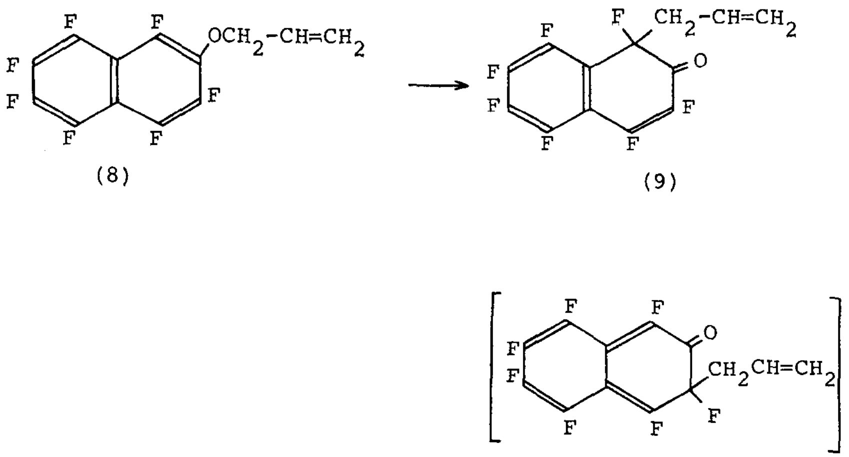


Scheme 2

(prop-2-enyl)-cyclohexa-2,5-dienone has been obtained from (1) via (2) followed by a Cope rearrangement [4]. In this paper, we report the isolation of the first polyfluoro Claisen-rearrangement product, 1,3,4,5,6,7,8-heptafluoro-1-(prop-2-enyl)-naphthalen-2-one, and the study of its photo- and thermally-induced reactions.

RESULTS AND DISCUSSION

1,3,4,5,6,7,8-Heptafluoro-2-naphthyl prop-2-enyl ether (8), prepared by the base-catalysed reaction of 1,3,4,5,6,7,8-heptafluoro-2-naphthol [5] with prop-2-enyl bromide, was ready isomerised to 1,3,4,5,6,7,8-heptafluoro-1-(prop-2-enyl)-naphthalen-2-one (9) in refluxing xylene over 2.5 h. (Scheme 3).



(8)

(9)

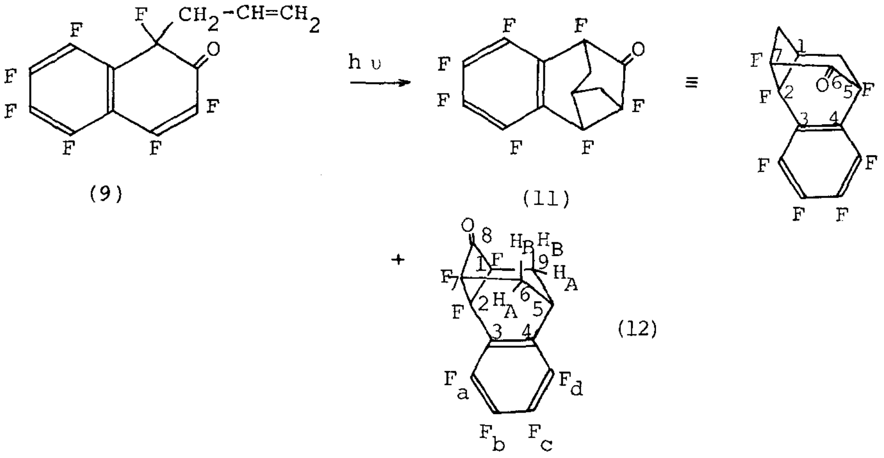
(10)

Scheme 3·

The structure of (9) was deduced from its ^{19}F n.m.r. spectrum which showed only one large peri J_{F-F} coupling constant ($J_{F-4,F-5}$ 75.7 Hz), whereas if the prop-2-enyl group had migrated to position 3 [to give (10)], two large peri J_{F-F} coupling constants would have been expected. A previous example of the formation of a stable dienone from a Claisen Rearrangement involves the conversion of 1-(prop-2-enyl)-2-naphthyl prop-2-enyl ether to 1,1-di(prop-2-enyl)naphthalen-2-one in 55% yield [6].

Photolysis of the naphthalene-2-one (9) at 350 nm. for 21 h. in acetonitrile gave complete conversion to two compounds which have been identified as 2,5,7-trifluoro-3,4-(tetrafluorobenzo)-tricyclo[3.3.1.0^{2,7}]non-3-en-6-one (11) (3 parts) and 1,2,7-trifluoro-3,4-(tetrafluorobenzo)tricyclo[3.3.1.0^{2,7}]non-3-en-8-one (12) (1 part) (Scheme 4). The separation of (11) and (12) by fractional recrystallisation was most effectively performed following their formation by the photolysis of (9) in cyclohexane.

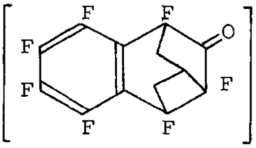
Compound (12) was readily recognised as the tetrafluorobenzo-analogue of (4) by ^{19}F n.m.r. and infra-red spectroscopy. The absorption centred at 185.1 p.p.m. and which accounted for two fluorines was a doublet and not two separate absorptions, since the separation did not increase when the spectrum was run in turn at 56.4 and 84.67 MHz. This showed that the molecule contained two magnetically equivalent fluorine atoms in positions related through a plane of symmetry, and identified them as F-1 and F-7 [cf. 193.5 p.p.m. for the corresponding



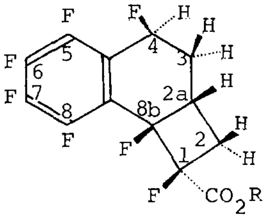
Scheme 4

absorption in (4)]. The highest signal at 208.7 p.p.m. was assigned to the bridgehead fluorine F-2 (a doublet due to peri coupling $J_{F-2,Fa}$ 45 Hz) [cf. 218 p.p.m. in (4)]. The strong absorption at 1848 cm.$^{-1}$ in the i.r. spectrum was due to the C=O at C-8 [cf. 1840 cm.$^{-1}$ in (4)]. Compound (12) formed the corresponding 8,8-diol (12a) with water, which was relatively unstable in comparison with the 8,8-diol hemihydrate formed by (4) [2].

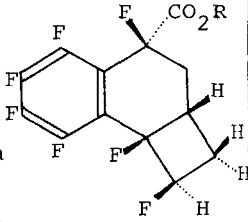
Compound (11) was one of the two expected [2+2] photochemically-allowed adducts. It was distinguished from the alternative adduct (13) by converting it into a separable mixture of isomers (14c) and (15c), via a haloform-type cleavage reaction with caustic soda [to give (14a) and (15a)] and acidification and methylation of the resulting carboxylic acids (14b) and (15b) with diazomethane. In principle two <u>pairs</u> of esters: (14c) and (15c), and (16) and (17) could be formed from the precursors (11) and (13) respectively. To distinguish between these two pairs we have compared n.m.r. coupling-constant data of (14c) with values known for compound



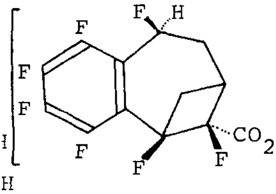
(13)



(14a) R = Na
(14b) R = H
(14c) R = Me



(15a) R = Na
(15b) R = H
(15c) R = Me



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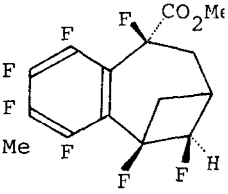

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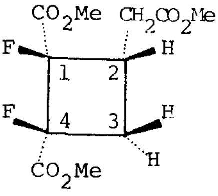


(18)

$J_{F-1\beta,H-2\beta} = 21$ Hz

$J_{F-4\beta,H-3\beta} = J_{F-4\beta,H-3\alpha} = 26$ Hz

$J_{F-1\beta,F-4\beta} \sim 0$ Hz

(18) as an appropriate model[3]. No model is available for an unequivocal assignment of the structure of (15c), but if the structure of one of the compounds of the pair of isomers is known, the structure of the other follows automatically. Furthermore, a chemical confirmation of the structures of (14a) and (15a) has been carried out.

Broad band decoupling of all the protons _except_ gem C$\underline{H}$F in the ^{19}F n.m.r. spectrum distinguished the non-aromatic fluorine atoms in (14c). The absorption at 140.3 p.p.m. (triplet J = 20,20) collapsed to a doublet which must be due to a peri J_{F-F} = 20 Hz (the aromatic fluorine having the additional coupling being the absorption at 137.8 p.p.m. which is a quartet). The broad triplet of doublets (J = 50; 42; 20

Hz) at 161.9 p.p.m. collapsed to a doublet ($J_{gem\ FH}$ 50 Hz) while the sharp triplet at 180.8 p.p.m. (J = 25; 25 Hz) collapsed to a singlet. The only structure compatible with the splitting patterns of these non-aromatic fluorine atoms, the magnitude of the coupling constants, and the behaviour on broad-band decoupling of the protons is (14c), derived from isomer (11), not (13); the assignments are given in the Experimental Section.

An interesting consequence of structure (14c) is the large value of $J_{F-4\beta,H-3\alpha}$ 42 Hz and also the absence of peri-coupling $J_{F-4\beta,F-5}$. This can be explained on the basis of one rigid conformation, a model of which indicates F-4β to be trans-peri-planar to H-3α and orthogonal to the aromatic ring; the relatively small peri-coupling $J_{F-8,F-8\beta}$ is also evident from this model. A large (30 Hz) trans vicinal J_{F-H} has been observed previously in syn-1,2-chlorofluorocyclohexane in a frozen conformation at low temperature [7], while theoretical calculations in substituted ethanes predict values for vicinal J_{HF}, from 37 to 62 Hz for a dihedral angle of 180° between the CH and CF bonds [8].

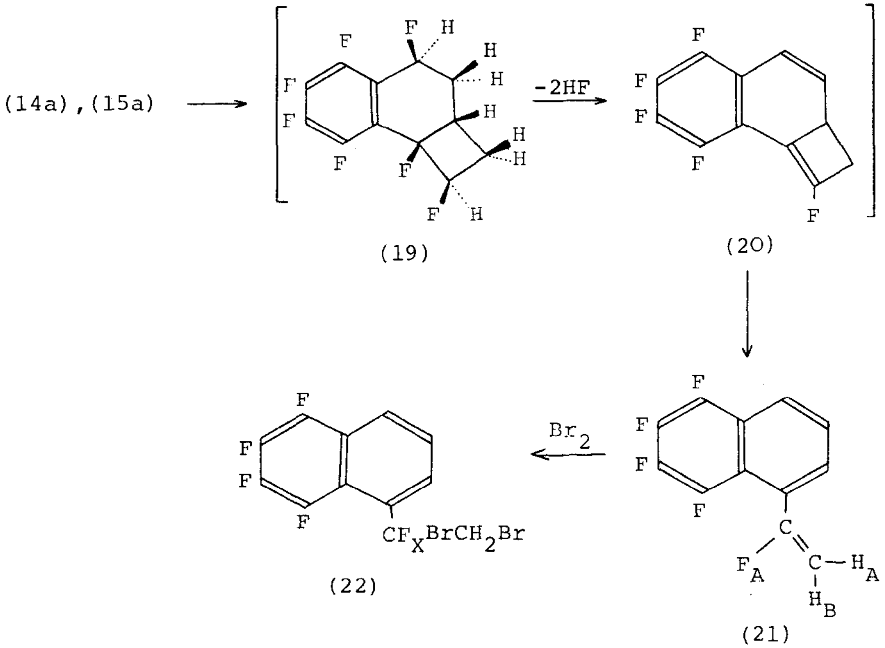
In spite of superficial structural similarities between (14c) and (15c) there is no consistency in either their coupling constant data or in their chemical shift data for the three non-aromatic fluorines. Broad band decoupling of all the protons except gem C$\underline{H}$F in the ^{19}F n.m.r. spectrum again distinguished the non-aromatic fluorine atoms. Only the broad triplet at 170.1 p.p.m. could be assigned unequivocally - to F-1β, in which the associated coupling constants were $J_{F-1\beta,H-1\alpha}$ 47 Hz and $J_{F-1\beta,H-2}$ 39 Hz for one of the protons at H-2 ($J_{F-1\beta,H-2}$ ∿ 0 Hz for the other proton at H-2).

The mass spectra of isomers (14c) and (15c), however, were very similar. Both showed mass 238 as their base peak, equivalent to the loss of a fragment mass 104 (corresponding to $CH_2=CFCO_2Me$) from the parent ion. The loss of such a fragment can readily be envisaged from this pair of compounds, but only from (17) of the other pair (16) and (17).

Chemical confirmation for the correct assignment of the structures of (14c) and (15c) came from the attempted decarboxylation in refluxing ethylene glycol of the mixture of the salts (14a) and (15a) resulting from the haloform-type cleavage of (11). The only product isolated (and in < 0.5% yield) was 1-(1-fluorovinyl)-5,6,7,8-tetrafluoronaphthalene (21 in Scheme 5) which was identified by mass spectroscopy, elemental analysis and n.m.r. spectroscopy. The significant absorptions in the ^{19}F n.m.r. spectrum were a low field fluorine at 83.3 p.p.m. due to F_A (triplet of doublets, $J_{F_A,F-8}$, 45 Hz; J_{F_A,H_A}, 45 Hz; J_{F_A,H_B}, 13 Hz) coupled to a fluorine at 143.0 p.p.m. due to F-8 (doublet of triplets: J_{F-8,F_A} 45 Hz; $J_{F,F(ortho)} = J_{F,F(para)} = 16$ Hz). The ^1H n.m.r. spectrum showed three protons centred at ca. 7.7 p.p.m. (aromatic protons) and two protons (the AB of an ABX system) centred at ca. 4.9 p.p.m. (vinylic protons) with J_{F_A,H_A} 45 Hz J_{F_A,H_B} 13 Hz and J_{H_A,H_B} 3 Hz. Compound (21) reacted with bromine in carbon tetrachloride at room temperature to give the dibromo compound (22). The ^1H n.m.r. of this compound showed three structurally adjacent protons in the aromatic region and a complex band from the two protons of the CH_2-group which on decoupling F_X simplified to a simple AB spectrum.

The naphthalene compound (21) can only arise from precursors having the carbon skeleton found in (14a) and (15a). A plausible reaction sequence leading to (21) is shown in Scheme (5). The bridgehead alkene (20) will be highly unstable and the probability of it being formed in preference to the two alternative modes of loss of HF from the cyclobutane part of molecule (19) will be very low and would account for the very low yield of (21). However, of the three possible cyclobutene intermediates which could be derived from (19), the only stable product under the prevailing vigorous reaction conditions will be the ring-opened compound (21) [the other products would be a benzocyclooctatetraene and a 1,2-ethanonaphthalene which would ring-open to a highly reactive and polymerisable naphthoquinodimethane derivative].

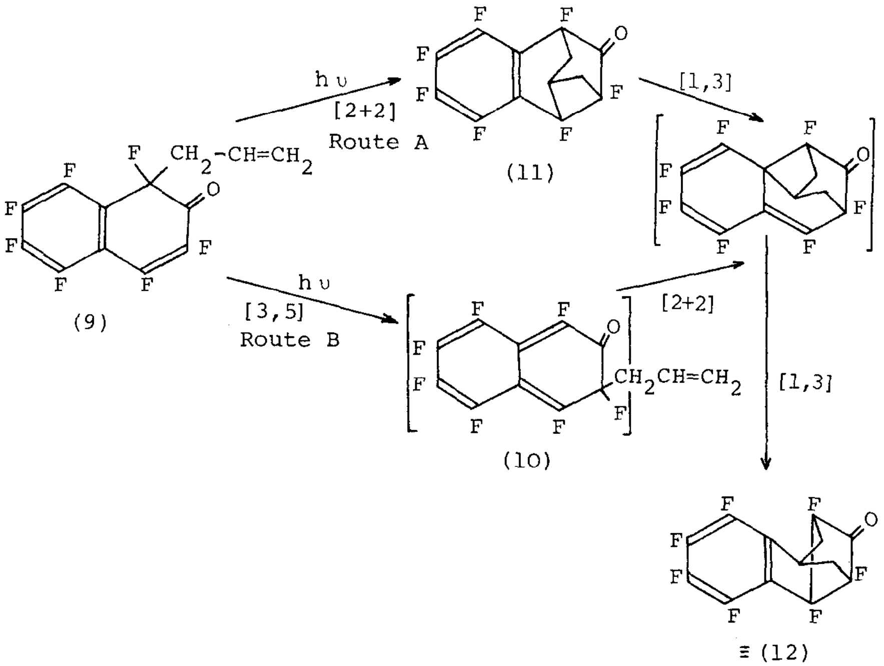
The formation of the symmetrical ketone (12) was unexpected. Two mechanisms compatible with the theory of photochemically-induced sigmatropic shifts are possible (Scheme 6). We have



Scheme 5

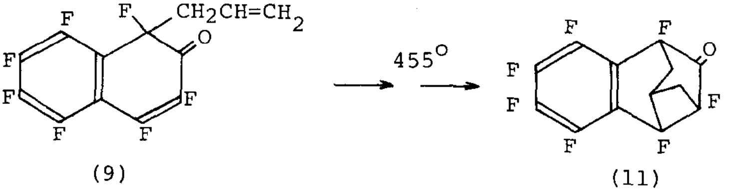
discounted Route A since no reaction occurred when (11) was photolysed under conditions used to convert (9) into (11) and (12). Consequently we propose Route B involving an initial [3,5]-shift as the reaction pathway.

It is remarkable that only one photochemically allowed [3,5]-sigmatropic shift proceeding suprafacially on both components has been identified previously [9]: the conversion of 2,6-dimethylphenyl[3-^{14}C]prop-2-enyl ether into an approximately equal mixture of 2,6-dimethyl-4-[(1-^{14}C]-prop-2-enyl)phenol (via the [3,5]-shift) and 2,6-dimethyl-4-([3-^{14}C]prop-2-enyl)phenol (by a competing mechanism involving two thermally allowed [3,3]shifts [10]). Thermally initiated [3,5] shifts should proceed suprafacially on one component and antarafacially on the other and examples of reactions involving such a shift have been proposed recently [11].



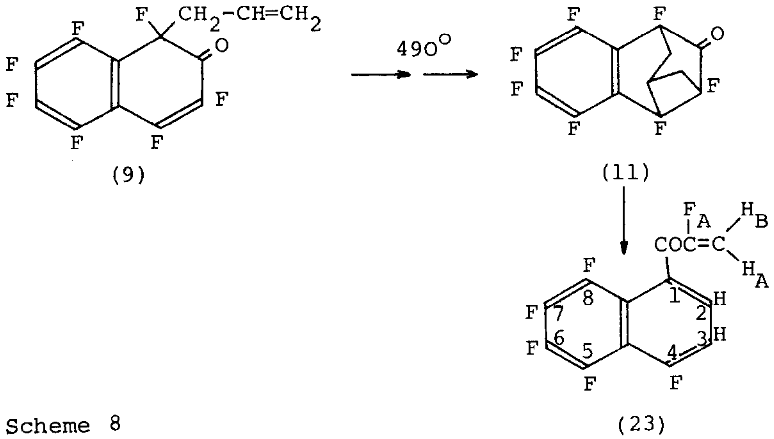
Scheme 6

The pyrolysis of the naphthalen-2-one (9) at 455° through a silica tube loosely packed with quartz wool gave a mixture of 1,3,5,6,7,8-heptafluoronaphthol and the previously prepared photo-product (11) in low yield. The formation of the last compound must arise by a non-concerted [2 + 2] cycloaddition reaction (Scheme 7). At 490° the naphthalen-2-one (9) gave 1-fluorovinyl 4,5,6,7,8-pentafluoro-1-naphthyl ketone (23)



Scheme 7

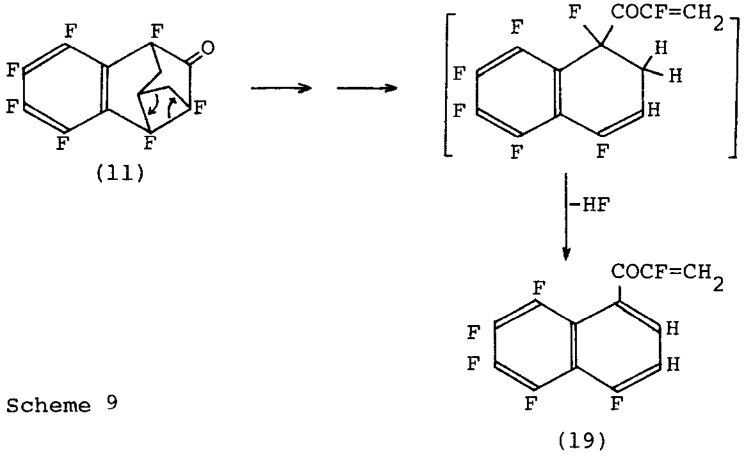
in low yield, but an improved conversion utilised compound (11) as the starting material (Scheme 8).



Scheme 8

The structure of (23) (having M^+ 290, starting material - HF) was determined from spectroscopic data. The vinylic fluorine was identified as the absorption at 115.8 p.p.m., a doublet of doublets which collapsed to a singlet on broad band decoupling of hydrogen (J_{F_A,H_A} 46 Hz; J_{F_A,H_B} 14 Hz). The absorption at 112.7 p.p.m. was assigned to F-4 from both the presence of a large peri coupling ($J_{F-4,F-5}$ 68 Hz) and the removal of the fine structure on the doublet (due to $J_{F-4,H-3}$ and $J_{F-4,H-2}$) by decoupling the protons.

The mechanism proposed for the formation of (23) is shown in Scheme 9. Previously, a related 1-fluorovinyl ether had been obtained by the pyrolysis of pentafluorophenyl prop-2-enyl ether [12].



Scheme 9

EXPERIMENTAL

^{1}H n.m.r. (90 MHz) and ^{19}F n.m.r. (84.67 MHz) spectra were obtained with a Brücker HX-90E spectrometer. Chemical shifts, δ_F are upfield from internal $CFCl_3$ reference (unless otherwise stated); δ_H are downfield from internal TMS.

1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-enyl ether (8).

Heptafluoronaphth-2-ol (90.0 g), prop-2-enyl bromide (60 ml) and anhydrous potassium carbonate (90 g) in dry acetone (900 ml) were heated under reflux and stirred for 18 h. The mixture was filtered, the volatile liquids distilled from the filtrate and the residue was distilled in steam to give a mixture of the ether and water (7 dm^3). The organic layer was separated and the aqueous layer was extracted with ether (3 x 300 ml). The combined organic materials were dried ($MgSO_4$), and the solvent evaporated to give 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-enyl ether (8) b.p.83.5° at 0.01 mm. Hg (66.0 g) [Found: C, 50.5; H, 1.6%; M$^+$, 310. $C_{13}H_5F_7O$ requires C, 50.34; H, 1.62%; M, 310].

1,3,4,5,6,7,8-Heptafluoro-1-(prop-2-enyl)-naphthalen-2-one (9).

The ether (8) (25.0 g) was heated in xylene (60 ml) at 130-135° for 2.5 h. and the solvent removed by distillation under high vacuum. The residue was washed with petroleum ether (b.p. 40-60°) (20 ml) and the crude naphthalenone was sublimed (0.005 mm Hg, 48-50°) and recrystallised three times from petroleum ether (b.p. 40-60°) to give pure 1,3,4,5,6,7,8-heptafluoro-1-(prop-2-enyl)-naphthalen-2-one (9) (16.0 g) m.p. 57-59°. [Found: C, 50.0; H, 1.4%; M$^+$, 310. $C_{13}H_5F_7O$ requires C, 50.34; H, 1.6; M, 310]; υ_{max}: 1708 (C=O) and 1670 cm^{-1} (CF=CF); δ_F ($CDCl_3$) 122.6 (F-4); 135.0 (F-8); 138.9 (F-5); 148.3 (F-7); 150.4 (F-6); 155.4 (F-1); 157.0 ppm (F-3) with external $CFCl_3$ reference. $J_{(F-1,F-8,\ peri)}$ 25 Hz; $J_{(F-4,F-5,\ peri)}$ 75.7 Hz

Photolysis of 1,3,4,5,6,7,8-heptafluoro-1-(prop-2-enyl)-naphthalen-2-one (9)

The naphthalenone (9) (20.0 g) dissolved in spectrochemical grade cyclohexane (600 ml) in a pyrex tube (5 cm. diameter x 45 cm.) was irradiated for 68 h. using a 350 nm lamp in conjunction with a 340 nm filter solution (56 g NaBr, 0.3 g $Pb(NO_3)_2$ in 100 ml water). The crystalline solid which precipitated was filtered off and recrystallised three times from benzene-petroleum ether (b.p. 40-60°) and sublimed to give 2,5,7-trifluoro-3,4-(tetrafluorobenzo)-tricyclo[3.3.1.$0^{2.7}$]-non-3-en-6-one (11) (8.5 g) m.p. 137-139°. [Found: C, 50.0; H, 1.3%; M^+, 310. $C_{13}H_5F_7O$ requires C, 50.34; H, 1.62%; M, 310]; υ_{max}: 1775 (C=O) cm^{-1} $\delta_F[CDCl_3]$ overlapping multiplets centred at 145.7 (F_a and F_d); 152.9, 153.9 (F_b, F_c both triplets) 174.0 (F-7,multiplet): 185.7 (F-5,doublet); 199.3 ppm. (F-2,doublet of doublets), $J_{(F_a,\ F\text{-}2,\ peri)}$ 46 Hz; $J_{(F_d,\ F\text{-}5,\ peri)}$ 45 Hz; $J_{(H\text{-}1,F\text{-}2)}$ 14 Hz.

The solvent was evaporated from the filtrate from the photolysis reaction and a ^{19}F n.m.r. analysis of the residue (8.5 g) showed that in addition to (11), there was present a second photoproduct (12) to the extent of 50% [20% in the overall product]. Compound (12) was isolated from the mixture by the following procedure. The mixture was recrystallised from benzene-petroleum ether (b.p. 40-60°) and the solid was then boiled with water and filtered. By this treatment (11) is believed to be unchanged while (12) is hydrated to the 8,8-diol. This product was boiled with CCl_4 to dissolve (11) and the undissolved solid [crude hydrated (12)] was filtered off. This material was recrystallised (twice) from benzene-petroleum ether [b.p. 40-60°] and finally sublimed in vacuo at 100°/0.05 mm. to give 1,2,7-trifluoro-3,4-(tetrafluorobenzo)-tricyclo[3.3.1.$0^{2,7}$]-non-3-en-8-one (12) (1.3 g), m.p. 122-123°. [Found: C, 50.3; H, 1.4; M^+ 310. $C_{13}H_5F_7O$ requires C, 50.3; H, 1.6%; M, 310]; υ_{max}: 1848 cm^{-1} (C=O). $\delta_F[(CD_3)_2CO]$ overlapping multiplets centred at 147.0 (F_a and F_d); 155.9, 157.6 (F_b and F_c,both triplets); 185.1 (F-1 and F-7 a doublet unchanged using a 56.4 MHz ^{19}F

spectrometer) intensity 2; 208.7 ppm (F-2,doublet) intensity 1. $\delta_H[(CD_3)_2CO]$ 2.05 (H-6A and H-9A showing splittings of 14 and 17 Hz); 3.08 ppm (H-6B and H-9B showing a splitting of 14 Hz); 3.92 ppm (H-5,broad singlet), $J_{(F_a, F-2)}$ 45 Hz.

Photolysis of the naphthalenone (9) (0.48 g) in acetonitrile (10 ml) for 21 h. as before and analysis of the product by ^{19}F n.m.r. showed the presence only of compound (11) 75% and the symmetrical ketone (12) (25%).

Hydration of Symmetrical Tricyclic Ketone (12).

The tricyclic ketone (0.3 g) was dissolved in boiling water and allowed to crystallise. The crystalline material was filtered and dried in vacuo to give 1,2,7-trifluoro-3,4-(tetrafluorobenzo)tricyclo[3.3.1.0^{2,7}]non-3-ene-8,8-diol (12a)m.p. 117-119^{o} [Found: C, 47.47; H, 2.34%. $C_{13}H_7F_7O_2$ requires C, 47.57; H, 2.15%]. υ_{max} 3400 cm^{-1} (OH). Sublimation of (12a) at 110^{o}/0.005 mm Hg over P_2O_5 gave the ketone (12), identified by i.r.

Hydrolysis of 2,5,7-trifluoro-3,4(tetrafluorobenzo)-tricyclo [3.3.1.0^{2,7}]non-3-en-6-one (11).

The photoproduct (11) (3.29 g) was refluxed in caustic soda (57 ml; 0.20 M) for 1.5 h. The solution was cooled and extracted with ether (3 x 100 ml), and the solvent was evaporated from the dried ($MgSO_4$) extracts to give unreacted starting material (11) (1.17 g) which was identified by i.r. The aqueous alkaline layer was acidified (4M; HCl), extracted with ether, and solvent evaporated from the dried ($MgSO_4$) extracts to give a viscous liquid (2.03 g) containing compounds (14b) and (15b). Treatment of this mixture with diazomethane in ether and removal of the excess diazomethane and solvent by distillation left a viscous yellow oil (2.42 g) which was partially separated by chromatography (silica, 2.4 x 90 cm, $CHCl_3/CCl_4$ 3:2 v/v) into two fractions: fraction (i) (1.28 g), the ^{19}F n.m.r. of which indicated that it was a 50:50 mixture of isomers (14c) and (15c); and fraction (ii) (0.69 g) b.p. 99-100^{o} at 0.01 mm Hg, which contained 95% (14c) and 5% (15c). Further purification of this fraction using thick layer chromatography on silica and the same solvent system as before gave pure 1β,4β,5,6,7,8,8bβ-heptafluoro-1α-methoxycarbonyl-8b,2a,3,4-tetrahydro-8bα,2aα-ethanonaphthalene (14c) as a viscous oil. [Found: C, 48.8; H, 2.9%; M^+ 342. $C_{14}H_9F_7O_2$ requires C, 49.1; H, 2.6%; M, 342] υ_{max} 1750 cm^{-1} (C=O) with a less intense peak at 1770 cm^{-1}. $\delta_F[(CD_3)_2CO]$ 137.8 (F-8, quartet); 140.3 (F-8bβ, triplet); 142.6 (F-5, triplet); 153.3 and 154.5 (unassigned F-6, F-7, both triplets); 161.9 (F-4β, broad triplet of doublets); 180.8 p.p.m. (F-1β, triplet); $\delta_H[(CD_3)_2CO]$, multiplet centred at 2.6 (2 x CH_2; CH); 3.68 (CH_3, singlet); 6.13 p.p.m. (H-4, doublet). $J_{(F-8,F-8b\beta)}$ 20 Hz; $J_{(F-8b\beta,H-2a\beta)}$ 20 Hz; $J_{(F-4\beta,H-4\alpha)}$ 50 Hz; $J_{(F-4\beta,H-3\alpha)}$ 42 Hz; $J_{(F-4\beta,H-3\beta)}$ 20 Hz; $J_{F-1\beta,H-2(\alpha \text{ and } \beta)}$ 25 Hz.

Re-chromatography of fraction (i) (1.28 g) (dry silica column 2.4 x 190 cm, $CHCl_3/CCl_4$ 3:2 v/v) gave after 14 h., a solid (0.65 g) which was recrystallised from petroleum ether (b.p. 60-80°), to give 1β,4β,5,6,7,8,8bβ-heptafluoro-4α-methoxycarbonyl-8b,2a,3,4-tetrahydro-8bα,2aα-ethanonaphthalene (15c), m.p. 105.5 - 106.2°. [Found: C, 49.4; H, 2.5%; M^+ 342. $C_{14}H_9F_7O_2$ requires C, 49.1; H, 2.6%; M^+ 342. υ_{max} 1765 cm^{-1} (C=O). $\delta_F[CDCl_3]$ 138.5 and 143.6 (unassigned F-5, F-8, broad multiplet and sharp multiplet respectively); 150.4 (F-4β OR F-8bβ, doublet $J_{F,H}$ 26 Hz); 151.7 and 152.5 (unassigned F-6, F-7, both triplets); 163.2 (F-8bβ OR F-4β; sharp multiplet); 170.1 p.p.m. (F-1β, broad triplet); $\delta_H[CDCl_3]$ multiplet centred at 2.67 (2xCH_2; CH); 3.68 (CH_3, singlet); 5.92 p.p.m. (F-1β, doublet). $J_{F-1\beta,H-1\alpha}$, 47 Hz; $J_{F-1\beta,H-2(\alpha \text{ or } \beta, \text{ unassigned})}$ 39 Hz.

Attempted decarboxylation of the mixed salts (14a) and (15a). Formation of 1-(1-fluorovinyl)-5,6,7,8-tetrafluoronaphthalene (21).

A crude mixture of carboxylic acids (14b) and (15b) (6.88 g), isolated as before from the photoproduct (11), was neutralised with an equivalent amount of sodium hydroxide

(103 ml; 0.20 M) and the crude dry salts [(14a) and 15(a)] were isolated by removal of water by distillation under reduced pressure. The mixture was heated under reflux with ethylene glycol (25 ml) for periods of 3 h., 19 h. and 61 h., after each period, the condenser being washed out with ether. The combined ether solutions were washed with water, dried ($MgSO_4$) and solvent evaporated. The residue (0.22 g) was sublimed at 50° at 0.05 mm and the white solid (0.022 g) was recrystallised three times from petroleum ether [b.p. $40-60^{\circ}$] at low temperature and sublimed as before to give 1-(1-fluorovinyl)-5,6,7,8-tetrafluoronaphthalene (21) (0.0098 g) m.p. $57-57.5^{\circ}$ [Found: C, 59.3; H, 2.0%; M^+, 244. $C_{12}H_5F_5$ requires C, 59.0; H, 2.1%; M^+, 244]; δ_F [$CDCl_3$], 83.3 (F_A, triplet of doublets); 143.0 (F-8, doublet of triplets); 149.7 (F-5, overlapping doublets); 157.7 and 158.2 p.p.m. (F-6, F-7, unassigned, both triplets); δ_H [$CDCl_3$] 4.67 (H_A, doublet of doublets); 5.01 (H_B, doublet of doublets); 7.54 (two protons); 8.02 (one proton). $J_{F_A,F-8}$ 45 Hz; J_{F_A,H_A} 45 Hz; J_{F_A,H_B} 13 Hz; J_{H_A,H_B} 3 Hz. Acidification of the main reaction-flask residue and extraction with ether gave a black tarry product (1.97 g) which contained none of compound (21) nor any other material which would elute on analytical T.L.C. (silica, solvent as before).

Treatment of the 1-fluorovinyl compound (21) (0.032 g) with bromine in carbon tetrachloride for one minute at room temperature, evaporation of excess solvent and halogen, and attempted sublimation of the residue at 90° at 0.05 mm Hg gave a colourless viscous oil of 1-(1-fluoro-1,2-dibromoethyl)-5,6,-7,8-tetrafluoronaphthalene (22). [Found: C, 35.5; H, 1.1%; M^+, 402. $C_{12}H_5Br_2F_5$ requires C, 35.7; H, 1.2%. M^+, 402 for ^{79}Br]. δ_F [$CDCl_3$] 95.4 (F_X broad unresolved multiplet); 130.2 (F-8, broadened triplet), 146.8 (F-5, very broad unresolved absorption); 154.8, 157.4 (F-6, F-7, unassigned, both triplets). δ_H [$CDCl_3$] 4.48 (A part of ABX, simple doublet); 4.86 (B part of ABX, doublet of doublet of doublets where J_{AB} = 12 Hz); 7.62, 8.01, 8.21 p.p.m. (triplet, doublet, doublet, respectively).

Attempted Photolysis of Photoproduct (11).

The photoproduct (11) (0.49 g) was dissolved in spectroscopic grade acetonitrile (10 ml) and irradiated in a 340 nm filter solution using a 350 nm UV lamp for 70 h. The solvent was evaporated and the residue in $(CD_3)_2CO$, examined by ^{19}F n.m.r. spectroscopy showed only unreacted starting material.

Pyrolysis of Photoproduct (11).

Compound(11) (1.5 g) was sublimed in vacuo (0.005 mm Hg) through a silica tube (1.5 cm diameter x 60 cm) loosely packed with quartz wool and heated to 490°, into a trap cooled in liquid air. The products were separated by column chromatography (silica, 2.4 x 90 cm, $CHCl_3/CCl_4$, 1:1) and the crude vinyl ketone (977 mg) was further purified by preparative scale thick layer chromatography (silica, $CHCl_3/CCl_4$, 1:1 v/v) to give an oily liquid which was sublimed at room temperature under high vacuum (0.005 mm Hg) to give a white solid. This was recrystallised three times from petroleum ether (b.p. 40-60°) to give 1-fluorovinyl 4,5,6,7,8-pentafluoro-1-naphthyl ketone (23) (263 mg) m.p. 70-71°. [Found: C, 54.0; H, 1.0%, M^+, 290. $C_{13}H_4F_6O$ requires C, 53.8; H, 1.4%; M, 290]; ν_{max}: 1700 (C=O) cm^{-1}; δ_F $[(CD_3)_2CO]$ 112.7 (F-4, doublet of multiplets); 115.8 (F_A, doublet of doublets); 137.1 (F-8, triplet); 144.3 (F-5, doublet of triplets); 155.2 and 157.0 ppm (F-6 and F-7, both triplets). δ_H $[(CD_3)_2CO]$ 5.45 (H_A); 5.77 (H_B); 7.46-7.88 ppm H-2 and H-3. $J_{(F-4,F-5,\ peri)}$ 68 Hz; $J_{(F_A,H_A)}$ 46 Hz; $J_{(F_A,\ H_B)}$ 14 Hz; $J_{(H_A,H_B)}$ 4.5 Hz.

Pyrolysis of the Naphthalenone (9).

(a) Isolation of the Vinyl ketone (23).

The naphthalenone (9) (2.45 g) was pyrolysed under vacuum (0.005 mm Hg) at 490° in the apparatus described previously. Separation of the complex mixture by column chromatography (silica, 2.4 x 90 cm, $CHCl_3/CCl_4$ 1:1 v/v) gave a fraction containing crude vinyl ketone (23) (157 mgm) which was further purified by preparative scale thick layer chromatography (silica, $CHCl_3/CCl_4$ 1:1 v/v) and identified by ^{19}F n.m.r. spectroscopy.

(b) Isolation of Photoproduct (11).

The naphthalone (9) (1.8 g) was pyrolysed under vacuum (0.005 mm Hg) at 455° and the complex mixture separated as before. The slowest eluting fraction contained a mixture of the 1,3,4,5,6,7,8-heptafluoro-2-naphthol and compound (11) (568 mg). Sublimation of this material at ca. 0.005 mm Hg gave two fractions: (i) (257 mg) (< 90°) being mainly the naphthol and (ii) (92 mg) (90°- 110°) mainly compound (11). The second fraction was leeched with petroleum ether (b.p. 60-80°) to give a solid (36 mg) identified by i.r. spectroscopy as compound (11). A further (63 mg) of photoproduct was obtained from the first fraction by washing it with Na_2CO_3 solution to remove naphthol.

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