

Partially Fluorinated Heterocyclic Compounds. Part 20.¹ Isomerisations of Pentafluorophenyl and 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ethers. Reactions of the Naphthyl Ether and 2-Fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]furan with 2,3-Dimethylbut-2-ene and with 3,3-Dimethylbut-1-ene

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Pentafluorophenyl prop-2-ynyl ether (1) has been isomerised to 4,5,6,7-tetrafluoro-2-fluoromethylbenzo[*b*]furan (2) in a liquid phase reaction while 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (3) gave 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (10) in both vapour phase and liquid phase reactions. Compounds (3) and (10) react with 2,3-dimethylbut-2-ene on heating to give 4,5,6,7,8,9-hexafluoro-2-(2,2,3-trimethylbut-3-enyl)naphtho[2,1-*b*]furan (16) and a small amount of 4,5,6,7,8,9-hexafluoro-2-(2,3,3-trimethylbut-1-enyl)naphtho[2,1-*b*]furan (15). Compound (10) reacts with 3,3-dimethylbut-1-ene at 25 °C in the presence of BF₃-diethyl ether to give 2-(3,4-dimethylpent-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]furan (19) and a small amount of (16). Both (3) and (10) on thermolysis with 3,3-dimethylbut-1-ene give (16) and smaller amounts of (19) and (15), compounds (15) and (16) arising *via* reaction with 2,3-dimethylbut-2-ene formed by isomerisation of the terminal alkene. 2-Chloromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]furan (11) has been prepared; this reacts with 3,3-dimethylbut-1-ene in the presence of ZnCl₂ to give (16), (15), and (19).

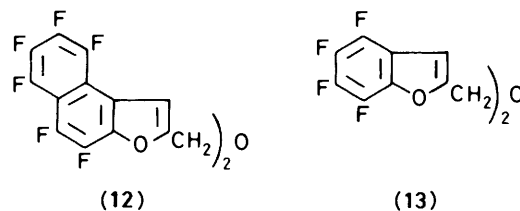
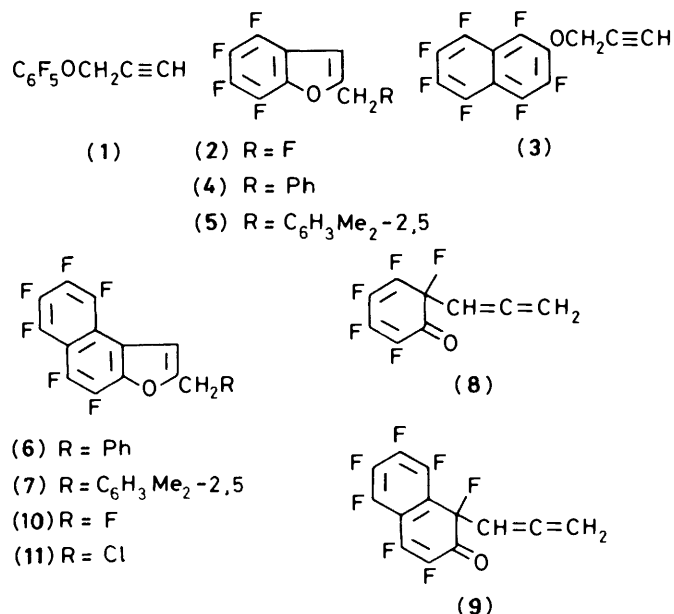
In a previous paper² the vapour-phase pyrolysis of pentafluorophenyl prop-2-ynyl ether (1) *in vacuo* at 370 °C was shown to give the isomerisation product (2) (8%). Moreover, the ether (1) and 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (3) both reacted with benzene and with *p*-xylene at *ca.* 140 °C in glass reaction vessels to give the furan derivatives (4) and (5) and (6) and (7) respectively. The formation of all these products was rationalised in terms of the intermediacy of Claisen rearrangement compounds (8) and (9) respectively; the naphthalenone (9) was even isolated in some cases.³ The mechanistic consideration of these reactions is considered in the following paper. Here, we report the isomerisation of (1) and (3) under different conditions, the thermolysis reactions of (3) with

two alkenes, and some reactions of 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (10) and 2-chloromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]furan (11) with the same alkenes.

Results and Discussion

1,3,4,5,6,7,8-Heptafluoro-2-naphthyl prop-2-ynyl ether (3) was distilled *in vacuo* through a silica tube packed with quartz wool at 360 °C to give a complex product from which was isolated 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (10) (43%) as the major component.⁴

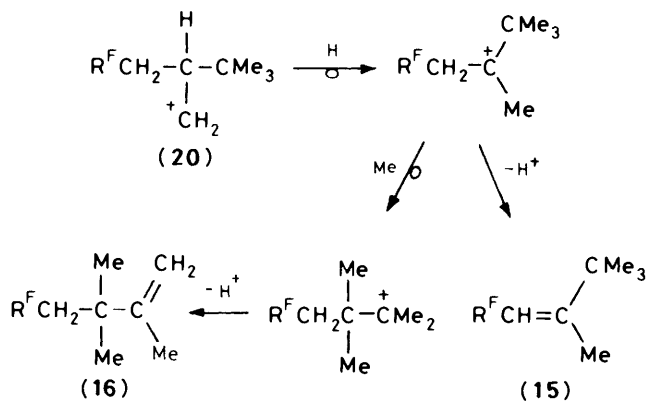
Previously the attempted isomerisations of both (3) and pentafluorophenyl prop-2-ynyl ether (1) in CF₂ClCFCl₂ as the solvent in glass apparatus at much lower temperatures (*ca.* 140 °C) had failed to give any of the respective 2-fluoromethyl derivatives (10) and (2).³ The ethers (12) and (13) respectively



were found in the products and it was proposed that the source of the oxygen was water actually formed *during* the experiment by the reaction of hydrogen fluoride (formed during the decomposition of the reaction mixture) with the glass walls of the reaction vessel. Consequently, subsequent experiments were carried out in nickel reaction vessels.

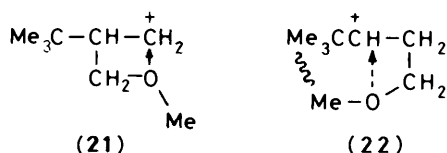
A solution of pentafluorophenyl prop-2-ynyl ether (1) in CF₂ClCFCl₂, heated in a nickel tube at 150 °C for 116 h gave the 2-fluoromethyl compound (2) (17%) and the ether derivative (13) (18%) which showed that water had been present during the reaction.

bring about this transformation, and the resulting internal alkene is expected to be considerably more reactive than its precursor, the terminal alkene, towards electrophilic or radical species. The ion (18) (Scheme 1) is the precursor to compounds (15) and (16), and could arise from the electrophilic attack on 2,3-dimethylbut-2-ene by a species designated $R^FCH_2^+$, or by an overall addition of R^FCH_2-F , compound (10), to the double bond *via* an unusual radical process* followed by loss of F^- . (ii) Alternatively, the products (15) and (16) are formed *via* the cation (20), (Scheme 4), which could arise *via* an anti-



Scheme 4.

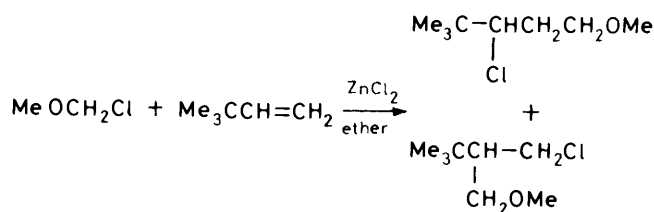
Markovnikov attack by $R^FCH_2^+$ on the terminal alkene, or again by the overall addition of R^FCH_2-F to the double bond *via* an unusual radical process* followed by loss of F^- . Russian workers have reported the formation of both Markovnikov and anti-Markovnikov addition compounds in the Friedel-Crafts reaction of chloromethyl methyl ether with 3,3-dimethylbut-1-ene⁷ (Scheme 5). No explanation was offered for the formation of the anti-Markovnikov adduct, but it could be due to the intermediacy of the stabilised cation (21). Molecular models show that steric interactions interfere with the secondary stabilising effect in the intermediate cation (22), the precursor to



the Markovnikov adduct. When these considerations are applied to the ion (20), an even more favourable stabilising interaction by the furan oxygen can be envisaged compared with the alternative possible cation.

We have devised experiments to assess the likelihood of the possibilities outlined in (i), for the naphthyl ether (3) and in (ii), for the 2-fluoromethyl compound (10). Control experiments with HF and 3,3-dimethylbut-1-ene heated under conditions identical with those used for the reaction with the naphthyl ether (3) and 3,3-dimethylbut-1-ene have shown that approximately four times as much 2,3-dimethylbut-2-ene would be produced than is necessary to yield the proportions of (15) and (16) actually found. It was assumed that *all* the HF which

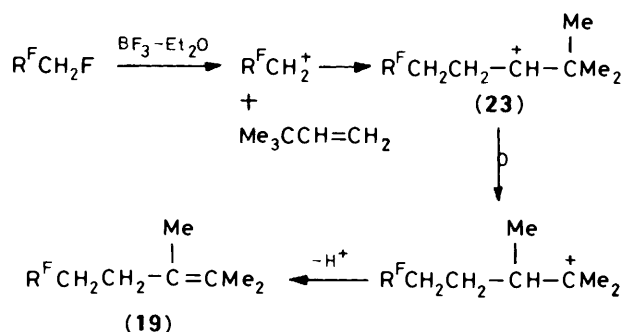
* It is important to note that a free-radical process was proposed to account for the formation of isomerisation products from 1-chloro-(bromo)-2-naphthyl prop-2-ynyl ether.⁵



Scheme 5.

could be produced in a typical experiment with the ether (3) brought about isomerisation of the terminal alkene; appropriate considerations of kinetics could then account for the formation of (15) and (16).

We have looked for significant formation of products derived *via* an anti-Markovnikov reaction [proposal (ii)] by treating 3,3-dimethylbut-1-ene with 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (10) in the presence of the Lewis acid boron trifluoride-diethyl ether at 25 °C. However, compound (19) (94 parts) was the major component identified, accompanied by only a small proportion (6 parts) of compound (16). Compound (19), the structure of which was assigned on the basis of its 1H n.m.r. spectrum, arises from an initial Markovnikov reaction to give the ion (23) which then undergoes a [1,2]-methyl shift followed by the loss of H^+ (Scheme 6). The analysis by g.l.c. of the separated *residual*



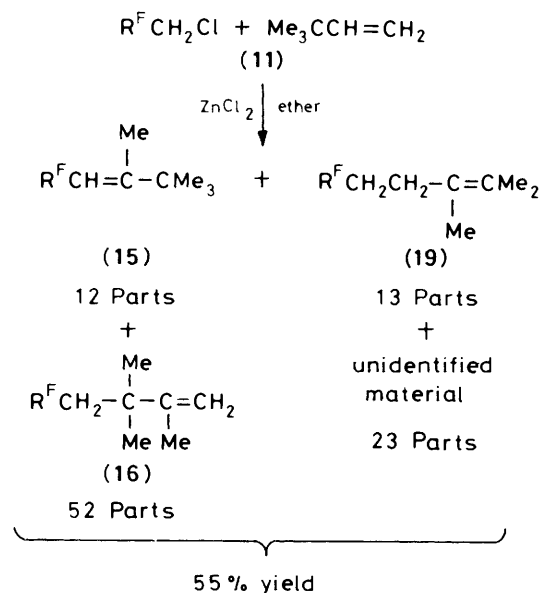
Scheme 6.

ether/unchanged alkene components of a reaction showed the presence of 2,3-dimethylbut-2-ene, *i.e.* the alkene was far *in excess* of that required to account for the amount of compound (16) in the reaction product. Control experiments at 25 °C also showed that 3,3-dimethylbut-1-ene is isomerised to 2,3-dimethylbut-2-ene by HF in the presence of boron trifluoride; more than sufficient of the internal alkene required to give the small proportion of compound (16) is produced by the amount of HF which would be produced from compound (10) in the actual experiment.

Thus it is now possible to account for the formation of all the three products identified in the reactions of both 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (3) and 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]furan (10) with 3,3-dimethylbut-1-ene. Compound (19) arose from a direct reaction with 3,3-dimethylbut-1-ene, whereas compounds (15) and (16) were actually produced from 2,3-dimethylbut-2-ene, which was formed by the isomerisation of the terminal alkene under the prevailing reaction conditions. The nature of the reacting species from experiments with the ether (3) is discussed in the following paper.

We have prepared 2-chloromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]furan (11) by a halogen exchange reaction with

the 2-fluoromethyl compound (10) using aluminium trichloride, in order to investigate its reaction with 3,3-dimethylbut-1-ene in the presence of zinc chloride. It was hoped to be able to effect both Markovnikov and anti-Markovnikov addition of the CH₂-Cl bond across the double bond of the terminal alkene, just as the Russian workers had done with CH₃OCH₂Cl.⁷ The result of the experiment is shown in Scheme 7. Overall



Scheme 7.

substitution of, rather than addition to the alkene had taken place. Compounds (15) and (16) which constituted the major fraction of the reaction product could have arisen via the anti-Markovnikov route (Scheme 4), but again, separation of the ether/unchanged alkene components from the mixture at the conclusion of the experiment, and analysis by g.l.c. showed the presence of 2,3-dimethylbut-2-ene. Clearly more than sufficient of the internal alkene had been produced from the 3,3-dimethylbut-1-ene during the reaction to account for the formation of the alkenes (15) and (16).

Experimental

¹H N.m.r. spectra (360 MHz) were obtained on the Bruker WH360 spectrometer located in the Chemistry Department at Edinburgh. ¹⁹F N.m.r. spectra were obtained with a Varian EM 360L spectrometer. Chemical shifts are downfield from internal SiMe₄ (δ_H), or upfield from internal CFCl₃ (δ_F). Ether refers to diethyl ether.

Vapour Phase Pyrolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether (3).—The ether (3) (0.175 g) was distilled by gentle warming through a silica tube (60 × 1.5 cm diam., the central section (20 cm) being packed with silica fibre) heated at 360 °C into a trap cooled by liquid air, connected to a high vacuum system (0.005 mmHg). Preparative thick layer chromatography of the crude product on silica using CCl₄-CHCl₃ (50:50 v/v) followed by sublimation at 50 °C/0.005 mmHg gave pure 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]-furan (10)⁴ (0.076 g, 43%).

Liquid Phase Isomerisations of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether (3).—(a) In *n*-decane. The ether (3) (3.92 g) and *n*-decane (15 ml) (freshly distilled from LiAlH₄)

were sealed in a nickel Carius tube (vol. 80 ml) under nitrogen and heated at 150 °C for 18 h. The products were washed from the tube with acetone, the solvents were distilled at 30 °C/0.01 mmHg and the crude products were separated by chromatography on silica (72 × 3 cm) using CCl₄-CHCl₃ (7:3 v/v) as the eluant to give two fractions. Fraction (i) (1.15 g), sublimed at 50 °C/0.05 mmHg to give the 2-fluoromethyl compound (10) (0.966 g, 25%), and the non-sublimable residue bis(4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]-furan-2-yl)methane (14)³ (0.065 g, 2%). Fraction (ii) (0.14 g), crystallised from light petroleum (b.p. 100–120 °C) to give bis(4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]-furan-2-ylmethyl) ether (12)³ (0.085 g, 2%).

(b) In CF₂CICFCl₂. The ether (3) (2.03 g) and CF₂CICFCl₂ (50 ml) were heated to 150 °C for 20 h as in (a) and the product was separated by chromatography to give (10) (1.653 g, 81%).

Liquid Phase Isomerisation of Pentafluorophenyl Prop-2-ynyl Ether (1) in CF₂CICFCl₂.—The ether (1) (2.83 g) and CF₂CICFCl₂ (30 ml) were heated at 150 °C for 116 h, as in (a) and the products were separated by chromatography on silica using CCl₄-light petroleum (b.p. 30–40 °C) (2:1 v/v) to give unchanged (1) (0.44 g, 16%), the 2-fluoromethyl compound (2)² (0.48 g, 17%), and the bis-ether (13)³ (0.49 g, 18%).

Thermolysis of 1,3,4,5,6,7-Heptafluoro-2-naphthyl Prop-2-ynyl Ether (3) with 2,3-Dimethylbut-2-ene.—(a) *Isolation of the products.* The ether (3) (5.98 g) and 2,3-dimethylbut-2-ene (11.0 ml, 7.8 g) were sealed in a nickel Carius tube and heated at 150 °C for 20 h. The products were washed from the tube with ether, the solvents were evaporated and the residue was separated by chromatography on silica using light petroleum (b.p. 30–40 °C). A mixture of three components (3.89 g, 54%) was rapidly eluted from the column and each component was obtained pure by further chromatography and fractional recrystallisation. The fastest moving component was 4,5,6,7,8,9-hexafluoro-2-(2,3,3-trimethylbut-1-enyl)naphtho[2,1-*b*]-furan (15), m.p. 153–154 °C [from light petroleum (b.p. 60–80 °C)] (Found: C, 61.55; H, 3.8%; M⁺, 372. C₁₉H₁₄F₆O requires C, 61.30; H, 3.76%; M, 372); δ_H(CDCl₃) 1.17 (s, 3 × Me), 2.12 (very narrow d, Me), 6.38 (q, vinylic C-H), and 7.12 (t, small long range coupling 3-furanyl C-H); δ_F(CDCl₃) 145.7–146.6 (br m), 151.1 (d), and 158.2–158.9 (br m) in the ratio 2:1:3 respectively; one *peri* J_{F-F} 70 Hz. The second fastest moving component was 4,5,6,7,8,9-hexafluoro-2-(2,2,3-trimethylbut-3-enyl)naphtho[2,1-*b*]-furan (16), m.p. 45–46 °C [from light petroleum (b.p. 60–80 °C)] (Found: C, 61.15; H, 3.8%; M⁺, 372. C₁₉H₁₄F₆O requires C, 61.30; H, 3.76%; M, 372); δ_H(CDCl₃) 1.17 (s, 2 × Me), 1.86 (dd, Me), 2.95 (s, CH₂), 4.72, 4.78 (2 × vinylic CH), and 6.96 (t, small long range coupling, 3-furanyl C-H); δ_F(CDCl₃) 145.7–146.7 (br m), 152.0–152.5 (br d) and 158.2–159.4 (br m) in the ratio 2:1:3 respectively; one *peri* J_{F-F} 65 Hz. The slowest of the three components was 4,5,6,7,8,9-hexafluoro-2-(2,2,3-trimethylbut-3-enyl)naphtho[1,2-*b*]-furan (17), m.p. 34.5–36.5 °C (Found: C, 61.29; H, 3.80%; M⁺, 372. C₁₉H₁₄F₆O requires C, 61.30; H, 3.76%; M, 372); δ_H(CDCl₃) 1.14 (s, 2 × Me), 1.83 (Me), 2.93 (CH₂), 4.67, 4.74 (2 × vinylic CH), and 6.66 (s, 3-furanyl C-H); δ_F(CDCl₃) 143.9 (br m), 146.8 (br m), 154.5–155.2 (br m) and 158.2–158.9 (br m) in the ratio 1:2:1:2 respectively; one *peri* J_{F-F} 68 Hz.

(b) *Determination of the product ratios.* The experiment described in (a) was repeated with the ether (3) (4.27 g) and 2,3-dimethylbut-2-ene (10 ml, 7.09 g). The mixture of the three fast eluting materials was separated by chromatography (2.78 g, 54%) and analysed by ¹H n.m.r. spectroscopy. The ratio of the three components (15):(16):(17) was 1:95:4.

*Reaction of 4,5,6,7,8,9-Hexafluoro-2-fluoromethylnaphtho[2,1-*b*]-furan (10) with 3,3-Dimethyl-1-ene in Boron Trifluoride-*

Diethyl Ether.—(a) *Isolation of 2-(3,4-dimethylpent-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (19).* A mixture of the 2-fluoromethyl compound (10) (0.498 g), diethyl ether (5 ml), 3,3-dimethylbut-1-ene (5 ml), and boron trifluoride-diethyl ether (2.5 ml) were stirred at 25 °C for 180 min. The solution was diluted with water, extracted with ether and the extracts dried (MgSO₄). Analytical t.l.c. of the product on silica using light petroleum b.p. (30–40 °C) as the solvent showed that there was a fast moving mixture, containing at least three components of similar retention time followed by a single, slower-moving component. The fast-moving components were separated from the major, slower-moving compound by sublimation of the crude product at 70–80 °C/0.005 mmHg. Flash chromatography⁸ of the sublimate (0.132 g, 22%) on silica using light petroleum (b.p. 30–40 °C) as the eluant and recrystallisation from light petroleum b.p. (40–60 °C) gave pure 2-(3,4-dimethylpent-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (19), m.p. 87.5–88.5 °C (Found: C, 61.5; H, 4.0%; *M*⁺, 372. C₁₉H₁₄F₆O requires C, 61.3; H, 3.8%; *M*, 372); δ_H(CDCl₃) 1.65 (m, small long range coupling, 2 × Me), 1.69 (m, small long range coupling, Me), 2.52 (t, CH₂), 2.93 (t, CH₂) and 6.97 (overlapping dd, small long range coupling, 3-furanyl C–H); δ_F(CDCl₃) 145.3–146.8 (br m), 151.9 (dd, *peri*-F *J*_{7,8} 62 Hz), 157.8–159.4 (br m), with intensities in the ratio 2:1:3 respectively. The slower-moving component was shown by ¹H n.m.r. and i.r. spectroscopy to be the bis-ether (12).³

(b) *Determination of the product ratios.* The experiment described in (a) was repeated at 25 °C with the fluoromethyl compound (10) (0.512 g) and gave a mixture containing at least three components (0.160 g, 26%); the ratio of identifiable compounds (16):(19):unknown compounds was 5:74:21.

(c) *Demonstration of the formation of 2,3-dimethylbut-2-ene during the reaction.* The experiment in (a) was repeated and the volatile products were evaporated and analysed by g.l.c. 2,3-Dimethylbut-2-ene was identified in the mixture.

3,3-Dimethylbut-1-ene in ether and BF₃-diethyl ether was isomerised to the 2,3-dimethylbut-2-ene by the addition of HF under the same conditions as in (a). Quantitative experiments showed that based on a typical experiment with compound (10), the amount of HF which would be released gave more than sufficient of the isomerised alkene to account for the small proportion of compound (16) formed in the reaction.

Thermolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether (3) with 3,3-Dimethylbut-1-ene.—The ether (3) (2.05 g) and 3,3-dimethylbut-1-ene (12 ml., 7.8 g) when sealed in a nickel Carius tube and heated at 150 °C for 20 h gave on work-up a mixture (1.07 g, 43%) which contained compounds (15), (16), (19), and unidentified material in the ratio 5:66:15:14 respectively, and the 2-fluoromethyl compound (10) (0.075 g, 3.5%).

Thermolysis of 4,5,6,7,8,9-Hexafluoro-2-fluoromethylnaphtho[2,1-b]furan (10) with Alkenes.—(a) *With 2,3-dimethylbut-2-ene.* The 2-fluoromethyl compound (10) (0.463 g) and 2,3-dimethylbut-2-ene (10 ml, 7.09 g) sealed in a nickel Carius tube and heated at 150 °C for 72 h gave on work-up a mixture (0.325 g, 58%) which contained compounds (15), (16), and unidentified material in the ratio 5:62:33 respectively. The small amount of unchanged material (10) which was present in the crude product (by t.l.c.) was not separated.

(b) *With 3,3-dimethylbut-1-ene.* (i) The 2-fluoromethyl compound (10) (0.704 g) and 3,3-dimethylbut-1-ene (10 ml) were heated at 150 °C for 20 h as in (a) and gave a mixture (0.0464 g, 5%) which contained compounds (15), (16), (19) and unidentified material in the ratio 18:43:14:25 respectively, and unchanged compound (10) (0.520 g, 74%).

(ii) Experiment (i) was repeated using compound (10) (1.177

g) and 3,3-dimethylbut-1-ene (12 ml) at 150 °C for 20 h and gave a mixture of (15), (16), (19) and unidentified material in the ratio 5.5:66:5.5:23 respectively (0.471 g, 33%). The unchanged starting material (10) present in the crude product was not separated.

(iii) Experiment (i) was repeated using (10) (0.449 g) and 3,3-dimethylbut-1-ene (12 ml) at 150 °C for 68 h and gave a mixture (0.108 g, 20%) which contained compounds (15), (16), (19) and unidentified material in the ratio 12:49:14:25 respectively and unchanged compound (10) (0.25 g, 56%).

Preparation of 2-Chloromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (11).—The 2-fluoromethyl compound (10) (0.175 g) dissolved in CF₂ClCFCl₂ (5 ml) was mixed with aluminium trichloride in acetonitrile (0.87M 1 ml). The solution was heated under reflux for 3 h, diluted with water, and extracted with ether. The extracts were dried (MgSO₄), the ether evaporated, and the crude product was sublimed at 60 °C/0.005 mmHg. The sublimate (0.129 g, 70%) was crystallised from light petroleum (b.p. 40–60 °C) to give 2-chloromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (11), m.p. 73.5–74 °C (Found: C, 48.4; H, 1.3. C₁₃H₃ClF₆O requires C, 48.1; H, 0.9%); δ_H(CDCl₃) 4.82 (s, CH₂) and 7.37 (t, 3-furanyl C–H); δ_F(CDCl₃) 144.5–146.5 (br m), 148.8 (dd, *peri*-F, *J*_{7,8} 67 Hz), and 154.9–158.1 (br m) in the ratio 2:1:3 respectively.

Reaction of 2-Chloromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (11) with 3,3-Dimethylbut-1-ene in the Presence of Zinc Chloride.—The chloromethyl compound (11) (0.1133 g, 0.35 mmol) in diethyl ether (1 ml) was added to anhydrous zinc chloride (0.091 g), weighed, and kept under a nitrogen atmosphere throughout the experiment. 3,3-Dimethylbut-1-ene (1 ml) was added and the mixture was heated under reflux (42 °C under N₂) for 22 h. The reaction mixture was diluted with water, the ether layer separated and the volatile components distilled at room temperature/0.05 mmHg, were shown by g.l.c. analysis to contain 2,3-dimethylbut-2-ene. The residue from the distillation was sublimed at 70–80 °C/0.005 mmHg and the sublimate (0.1031 g) was chromatographed on silica using light petroleum (b.p. 40–60 °C) as the eluant to give a mixture which contained compounds (15), (16), (19), and unidentified material in the ratio 12:52:13:23 respectively (by ¹H n.m.r.) (0.072 g, 55%). In this product the hydrogen at C-3 in the furan ring of the component assigned as compound (15) had δ_H 7.04 compared with δ_H 7.12 in the material isolated previously though the shifts of the other protons were essentially unchanged. This could be due simply to a concentration effect or possibly to it being a different geometrical isomer.

Isomerisation of 3,3-Dimethylbut-1-ene with HF.—A mixture of 3,3-dimethylbut-1-ene (10 ml, 6.53 g) and hydrogen fluoride (0.3 g) was heated in a nickel Carius tube at 150 °C for 20 h. The contents of the tube were diluted with water and the integrated ¹H n.m.r. spectrum of the organic phase showed that 24% isomerisation to 2,3-dimethylbut-2-ene had occurred.

In a typical reaction of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (3) with 3,3-dimethylbut-2-ene it was shown that the HF which would be produced would give more than sufficient 2,3-dimethylbut-2-ene to account for the formation of compounds (15) and (16).

Acknowledgements

We thank the S.E.R.C. for a research assistantship (J. R. C. and A. G. M.) and Dr. Ian Sadler, Edinburgh University for the ¹H n.m.r. spectra.

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Received 28th March 1985; Paper 5/522