

Pyrolyses of Pentafluorophenyl Prop-2-enyl and [2,3,3-²H₃]Prop-2-enyl Ethers. Formation of 1-Fluorovinyl 2,3,4-Trifluorophenyl Ketones *via* Internal Diels–Alder Reactions

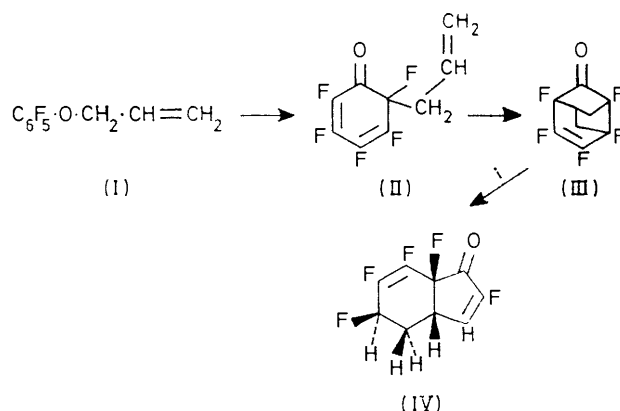
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The formation of 1-fluorovinyl 2,3,4-trifluorophenyl ketone (XIV) by pyrolysis of pentafluorophenyl prop-2-enyl ether (I) at 440 °C in the vapour phase is rationalised in terms of a reaction involving one of two possible internal Diels–Alder adducts (V) of the intermediate 2,3,4,5,6-pentafluoro-2-(prop-2-enyl)cyclohexa-3,5-dienone (II). The same 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 (XIV), a reaction which has been observed by using pentafluorophenyl [2,3,3-²H₃]prop-2-enyl ether (VI). This gives not only 1-fluoro[2,2-²H₂]vinyl 2,3,4-trifluoro[5-²H₁]-phenyl ketone (XVIII) (1 part), the product expected from 2-([1,1,2-²H₃]prop-2-enyl)cyclohexa-3,5-dienone (IX), but also 1-fluorovinyl 2,3,4-trifluoro[5,6-²H₂]phenyl ketone (XIX) (1 part), from 2-([2,3,3-²H₃]prop-2-enyl)cyclohexa-3,5-dienone (X), the relative proportions of the products indicating complete equilibration of (IX) and (X) before further reaction.

In a previous paper, the pyrolysis of pentafluorophenyl prop-2-enyl ether (I) at 480 °C was described.¹ One component of the complex mixture of products was 2,5β,6,7,7aβ-pentafluoro-3aβ,4,5,7a-tetrahydroinden-1-one (IV), the formation of which was rationalised on the basis of the isomerisation of one of two possible internal Diels–Alder adducts (III) from the initially formed Claisen rearrangement product (II) (Scheme 1).

The implication of the alternative internal Diels–Alder adduct (V) was only revealed by using the deuterium-labelled material pentafluorophenyl [2,3,3-²H₃]prop-2-enyl ether (VI). Not only was the [3,3aβ,5α-²H₃]ketone (VII) formed, but also the [3aβ,4,4-²H₃]ketone (VIII), in the ratio 9 : 10, respectively, and it was argued that while (VII) arose from the expected Claisen rearrangement material (IX), the formation of (VIII) required the 2,4-dienone (X) (Scheme 2). It was proposed that compound (X) arose from (XI), the second possible internal Diels–Alder adduct from (IX), by a stepwise rearrange-

ment, and moreover that the overall isomerisation represented by (IX) ⇌ (X) (the *ortho–ortho* rearrange-

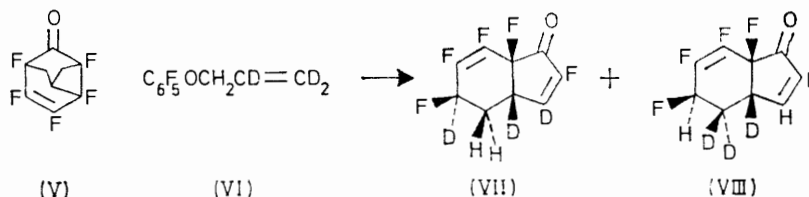


SCHEME 1 i, Ring cleavage and hydrogen transfer

ment) attained equilibrium very rapidly in comparison with the subsequent formation of products *via* the internal

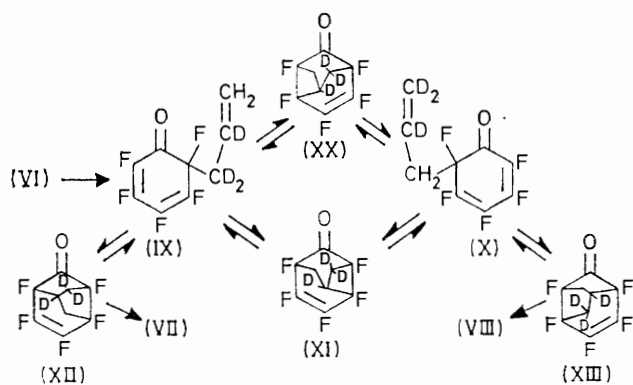
¹ G. M. Brooke, *J.C.S. Perkin I*, 1974, 233.

Diels–Alder adducts (XII) and (XIII). The presence of the unlabelled bicyclic ketone (IV) obviously fails to reveal the degenerate *ortho-ortho* rearrangement which must be proceeding *via* the internal Diels–Alder adduct



(V), but we have now isolated another material, from the pyrolysis of (I) at 440 °C, which can be related directly to (V).

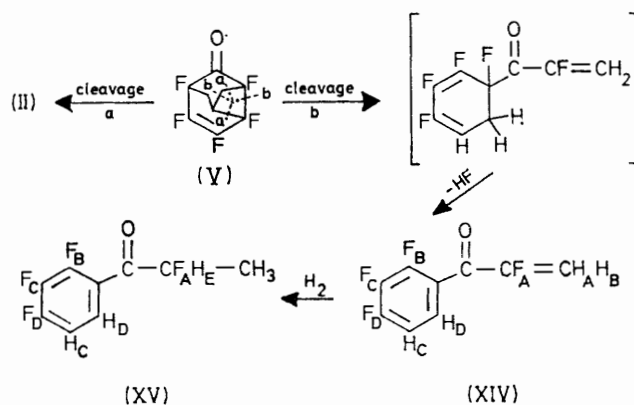
Prior removal of the ketone (IV) from the pyrolysis product and analysis of the residue by coupled g.l.c.–mass spectrometry showed the presence of a material with M^+ 204 (starting material –HF) present to the extent of *ca.* 40%. This material (which readily polymerised in air) was shown to be 1-fluorovinyl 2,3,4-trifluorophenyl ketone (XIV) on the basis of spectroscopic data and further chemical reactions. The u.v. and i.r. spectra were consistent with the presence of a conjugated ketone; the ^1H n.m.r. spectrum showed two aromatic



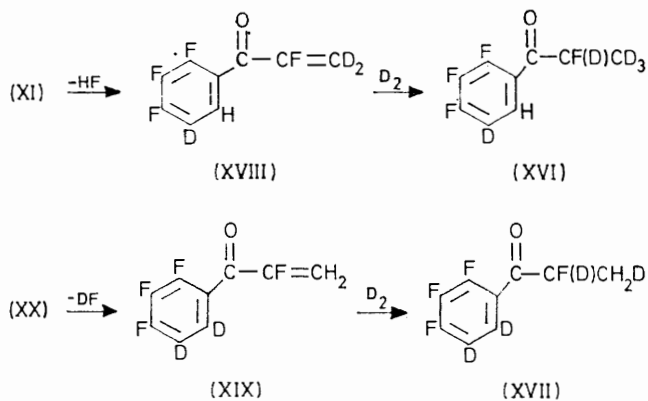
and two vinylic C–H absorptions; and the ^{19}F n.m.r. spectrum showed one vinylic fluorine and three aromatic C–F absorptions. Oxidation of compound (XIV) with fuming nitric acid gave a carboxylic acid identified unambiguously as 2,3,4-trifluorobenzoic acid on the basis of elemental analysis and mass spectrum and the presence of three fluorine absorptions in the ^{19}F n.m.r. spectrum, one absorption having two coupling constants of 20.5 Hz, each characteristic of two adjacent *ortho*-fluorine atoms. Catalytic hydrogenation of the ketone (XIV) gave the expected 1-fluoroethyl 2,3,4-trifluorophenyl ketone (XV). Both compounds (XIV) and (XV) showed large through-space F,F-coupling constants, $J(\text{F}_\text{A}, \text{F}_\text{B})$ 17.0 and 15.5 Hz, respectively, which indicate rigid conformations in these molecules.

The formation of the ketone (XIV) can be explained by invoking the opening of the four-membered ring of

the internal Diels–Alder adduct (V) by the mode alternative to the one involved in the degenerate *ortho-ortho* rearrangement, followed by loss of HF (Scheme 3). In order to determine the relative ease of cleavage of bonds



in order to simplify the ^1H n.m.r. analysis of the product. Two compounds (XVI) and (XVII) were obtained in the ratio 1:1.1, respectively (Scheme 4), which in turn showed the pyrolysis products to be the unsaturated ketone (XVIII) [from (XI)] and the unsaturated ketone (XIX), which must have been produced from the internal Diels–Alder adduct (XX) (see Scheme 2).



The isolation of the bicyclic ketones (VII) and (VIII) (1:1) in the same pyrolysis experiment, and the form-

ation of essentially identical amounts of unsaturated ketones (XVIII) and (XIX) indicate common precursors, namely the 2,4-dienones (IX) and (X). Furthermore, the equilibrium between these compounds, (IX) and (X), must be established very rapidly in comparison with reactions arising from the two possible types of internal Diels-Alder adducts [(XI) and (XX); and (XII) and (XIII)]. We conclude therefore that cleavage of bonds a in (V) is much easier than cleavage of bonds b.

EXPERIMENTAL

Pyrolysis of Pentafluorophenyl Prop-2-enyl Ether (I).—The ether (I) (19.4 g) was distilled during 4 h from a vessel at 70 °C through a silica tube (20 cm × 1.5 cm diam.) packed with silica fibre and heated to 440 °C, into a trap cooled by liquid air connected to a high vacuum system (0.001 mmHg). The liquid product (18.8 g) was cooled to -10 °C to precipitate 2,5β,6,7,7aβ-pentafluoro-3aβ,4,5,7a-tetrahydroinden-1-one (IV), which was filtered off, and the filtrate was washed with water to remove HF. Examination of this product by coupled g.l.c.-mass spectrometry (V.G. Micromass 12B instrument) indicated a complex mixture with one component, M^+ 204 (starting material -HF), present in significant amount (40%). Chromatography of the mixture (6.0 g) on silica (70 cm × 3.5 cm diam.) (carbon tetrachloride as eluant) gave an impure sample of this component, 1-fluorovinyl 2,3,4-trifluorophenyl ketone (XIV) (1.4 g), b.p. 42° at 0.03 mmHg, as a slow moving material which rapidly polymerised in the absence of solvent and so was immediately hydrogenated or oxidised. The ^{19}F n.m.r. spectrum [(CD₃)₂CO] showed signals at 115.1 (F_A), 128.1 (F_D), 134.2 (F_B), and 160.3 (F_C) p.p.m. upfield from internal CFCl₃ [$J(\text{F}_A, \text{anti-H}_A)$ 45.0, $J(\text{F}_A, \text{syn-H}_B)$ 12.0, $J(\text{F}_A, \text{F}_B)$ 17.0, $J(\text{F}_B \text{F}_C)$ 20.5, $J(\text{F}_B, \text{F}_D)$ 12.0, $J(\text{F}_B, \text{H}_C)$ 6.0, $J(\text{F}_B, \text{H}_D)$ 3.0, $J(\text{F}_C, \text{F}_D)$ 20.5, $J(\text{F}_C, \text{H}_C)$ 6.0, $J(\text{F}_C, \text{H}_D)$ 3.0, $J(\text{F}_D, \text{H}_C)$ 9.0, $J(\text{F}_D, \text{H}_D)$ 5.5 Hz]. The ^1H n.m.r. [(CD₃)₂CO] showed τ 2.3–3.3 (complex m, H_C and H_D), 4.38 (*anti-H*_A), and 4.43 (*syn-H*_B); ν_{max} 1 692 cm⁻¹ (C=O); λ_{max} (cyclohexane) 252 nm (ϵ 14, 700).

Pyrolysis of Pentafluorophenyl [2,3,3-²H₃]Prop-2-enyl Ether (VI).—The ether (VI) (6.0 g) was pyrolysed as in the previous experiment to give a product separated by chromatography on silica (CCl₄ as eluant) into 1-fluoro[2,2-²H₂]vinyl 2,3,4-trifluoro[5-²H₁]phenyl ketone (XVIII) and 1-fluorovinyl 2,3,4-trifluoro[5,6-²H₂]phenyl ketone (XIX) (0.8 g); this was *not* distilled, but was treated immediately with deuterium. The slower moving components on the column were eluted with ether and finally separated by preparative t.l.c. on Kieselgel GF₂₅₄ (chloroform as eluant) to give a mixture of [3,3aβ,5α-²H₃]-2,5,6,7,7aβ-pentafluoro- (VII) and [3aβ,4,4-²H₃]-2,5β,6,7,7aβ-pentafluoro-3a,4,5,7a-tetrahydroinden-1-one (VIII) in the ratio 1 : 1 {from the intensities of the ^1H n.m.r. signals [(CD₃)₂CO] at τ 4.65 and 7.59 respectively}.

1-Fluoroethyl 2,3,4-Trifluorophenyl Ketone (XV).—The crude vinyl ketone (XIV) (1.7 g) in ethyl acetate (30 ml) was

hydrogenated at atmospheric pressure over palladium-charcoal (0.5 g; 10% w/w) at room temperature until *ca.* 1 mol equiv. of gas had been absorbed. The catalyst was filtered off, the solution evaporated, and the residue purified by preparative g.l.c. (di-isodecyl phthalate, 178 °C) to give 1-fluoroethyl 2,3,4-trifluorophenyl ketone (XV), m.p. 46–47 °C (from ethanol-water) (Found: C, 52.7; H, 2.6; F, 36.1%; M^+ , 206; C₉H₈F₄O requires C, 52.4; H, 2.6; F, 36.8%; M , 206). The ^{19}F n.m.r. spectrum (CFCl₃) showed signals at 128.7 (F_D), 133.3 (F_B), 162.3 (F_C), and 184.4 (F_A) p.p.m. upfield from internal CFCl₃ [$J(\text{F}_A, \text{H}_B)$ 48.0, $J(\text{F}_A, \text{vic-H})$ 23.0, $J(\text{F}_A, \text{F}_B)$ 15.5, $J(\text{F}_B, \text{F}_C)$ 20.0, $J(\text{F}_B, \text{F}_D)$ 12.0, $J(\text{F}_C, \text{F}_D)$ 19.0, $J(\text{F}_C, \text{H}_C)$ 6.5, $J(\text{F}_C, \text{H}_D)$ 1.5, $J(\text{F}_D, \text{H}_C)$ 9.2, $J(\text{F}_D, \text{H}_D)$ 6.2 Hz]. The ^1H n.m.r. spectrum (CFCl₃) showed τ 2.52 (H_D), 2.90 (H_C), 4.54 (H_E), and 8.56 (CH₃) [$J(\text{CH}_E, \text{CH}_3)$ 7.0 Hz]; ν_{max} 1 705 cm⁻¹ (C=O).

Reactions of 1-Fluorovinyl 2,3,4-Trifluoro[5,6-²H₂]phenyl Ketone (XIX) and 1-Fluoro[2,2-²H₂]vinyl 2,3,4-Trifluoro[5-²H₁]phenyl Ketone (XVIII) with Deuterium.—The crude mixture of ketones (XVIII) and (XIX) (see above), in ethyl acetate, was treated at atmospheric pressure with deuterium over palladium-charcoal, and the product was isolated by preparative t.l.c. as before. The ^1H n.m.r. spectrum [(CD₃)₂CO] showed signals for ring protons H-6 and H-5 and side-chain protons H-1 and H-2, with relative intensities 1 : 0.23 : 1.71 : 2.19, which indicated the presence of both 1-fluoro[1,2,2-²H₄]ethyl 2,3,4-trifluoro[5-²H₁]phenyl ketone (XVI) and 1-fluoro[1,2-²H₂]ethyl 2,3,4-trifluoro[5,6-²H₂]phenyl ketone (XVII) in the ratio 1 : 1, respectively) in which 11% overall exchange of H for D at ring position 5 and 82% overall exchange of H for D at side-chain position 1 had occurred. A separate experiment showed that these exchange reactions could be induced on the silica by moisture in the environment (the silica, the solvent, or the atmosphere).

2,3,4-Trifluorobenzoic Acid.—The crude vinyl ketone (XIV) (0.14 g) was heated under reflux with nitric acid (10 cm³; 70% w/w) for 2 h. The mixture was diluted with water and extracted with ether, and the dried (MgSO₄) extracts were evaporated. Sublimation of the residue at 120 °C and 0.05 mmHg and recrystallisation from toluene-petroleum (b.p. 60–80 °C) gave 2,3,4-trifluorobenzoic acid (0.043 g), m.p. 136.5–137 °C (Found: C, 48.0; H, 2.0; F, 32.7%; M^+ , 176. C₇H₃F₃O₂ requires C, 47.7; H, 1.7; F, 32.3%; M , 176). The ^{19}F n.m.r. spectrum (Et₂O) showed signals at 130.4 (F-4), 132.1 (F-2), and 163.0 (F-3) upfield from external CFCl₃ [$J(\text{F-2}, \text{F-3})$ 19.0, $J(\text{F-2}, \text{F-4})$ 12.5, $J(\text{F-3}, \text{F-4})$ 19.0, $J(\text{F-2}, \text{H-5})$ 2.5, $J(\text{F-2}, \text{H-6})$ 7.0, $J(\text{F-3}, \text{H-5})$ 6.5, $J(\text{F-3}, \text{H-6})$ 2.5, $J(\text{F-4}, \text{H-5})$ 8.5, $J(\text{F-4}, \text{H-6})$ 6.0 Hz]. The ^1H n.m.r. spectrum (Et₂O) showed τ 2.52 (H-6) and 3.21 (H-5) (external Me₄Si standard) ($J_{5,6}$ 9.0 Hz); ν_{max} 1 690 cm⁻¹ (C=O).

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