

A New Route to the Rare Tricyclo[3.3.1.0^{2,7}]nonane Skeleton. Synthesis of 1,2,3,4,7-Pentafluorotricyclo[3.3.1.0^{2,7}]non-3-ene-8,8-diol Hemihydrate *via* Thermolysis of Pentafluorophenyl Prop-2-enyl Ether, and Related Studies

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Prolonged heating of pentafluorophenyl prop-2-enyl ether (1) in the vapour phase at 137–141 °C and hydration of the product gives a compound (10) incorporating the rare [3.3.1.0^{2,7}]nonane ring skeleton and containing a plane of symmetry. An analogous reaction occurs with pentafluorophenyl 2-methylprop-2-enyl ether. Some reactions of (10) are described.

THE flow pyrolysis of pentafluorophenyl prop-2-enyl ether (1) in the vapour phase at 440–480 °C has been shown to give the products (4)¹ and (6),² whose formation was rationalised in terms of reactions of both possible internal Diels–Alder adducts (3) and (5), respectively, of the intermediate 2,3,4,5,6-pentafluoro-6-(prop-2-enyl)cyclohexa-2,4-dienone (2) (Scheme 1). An analogous reaction scheme can be drawn up using pentafluorophenyl 2-methylprop-2-enyl ether.³

The tricyclic skeleton in (3) represents an entirely new ring system and even the tricyclo[3.3.1.0^{2,7}]nonane skeleton in (5) is very rare, only two syntheses having been described.^{4,5} The intermediate (5) is responsible for the degenerate *ortho-ortho* rearrangement [(2) \rightleftharpoons (7)] which has been identified using pentafluorophenyl [2,3,3-²H₃]prop-2-enyl ether;¹ Schmid originally invoked this ring skeleton to account for the equilibration of radioactivity between C-1 and -3 of the prop-2-enyl group during the thermolysis of 2,4,6-trimethylphenyl [3-¹⁴C]prop-2-enyl ether.⁶

In an attempt to isolate the proposed internal Diels–Alder intermediates (3) and (5), the ether (1) was heated in the vapour phase at a lower temperature (137–141 °C) for a longer time (13 days). Unchanged ether (1), 2,3,4,5,6-pentafluoro-4-(prop-2-enyl)cyclohexa-2,5-dienone (8) [previously prepared by pyrolysis of (1) at 365 °C],⁷ and an unidentified solid were removed from the product, and the residue was shown to be 1,2,3,4,7-pentafluorotricyclo[3.3.1.0^{2,7}]non-3-ene-8,8-diol hemihydrate (10) from the following data.

The i.r. spectrum showed strong absorptions at 3 550, 3 480, and 3 350 (O–H region), and at 1 758 cm⁻¹ (CF=CF); there was no absorption due to C=O, even though mass spectrometry showed *m/e* 224 as the highest mass peak, identical with that of the starting material. The ¹⁹F n.m.r. spectrum showed four absorptions centred at 140.6 and 164.5 (vinylic C–F), and 193.5 and 218.0 p.p.m. (bridgehead C–F) in the ratio 1:1:2:1, respectively. Significantly, the absorption centred at 193.5 p.p.m. was shown to be a doublet (*J* 18.0 Hz), and not two separate absorptions, by the failure to increase the separation 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. Determination of the complete molecular structure by X-ray crystallography showed that one molecule of water was associated with two *gem*-diol molecules.⁸ The elemental analysis, the integrated ¹H n.m.r. spectrum, and the molecular weight (by vapour phase osmometry) became meaningful with this structure.

The two magnetically equivalent fluorine resonances at 193.5 p.p.m. were assigned to F-1 and -7 and the absorption at the highest field to F-2. The ¹H n.m.r. spectrum showed a low field broad absorption at τ 6.13, characteristic of a bridgehead proton (H-5), and broad-band decoupling of this proton removed the broad doublet structure of the absorption at 140.6 p.p.m. in the ¹⁹F n.m.r. spectrum; this distinguished F-4 from F-3. The magnetically equivalent protons H-6 and -9, coupled

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

² G. M. Brooke and D. H. Hall, *J.C.S. Perkin I*, 1976, 1463.

³ G. M. Brooke and D. H. Hall, *J. Fluorine Chem.*, 1977, 10, 495.

⁴ W. Frostl and P. Margaretha, *Helv. Chim. Acta*, 1976, 59, 2244.

⁵ A. Kranz, *J. Amer. Chem. Soc.*, 1972, 94, 4020.

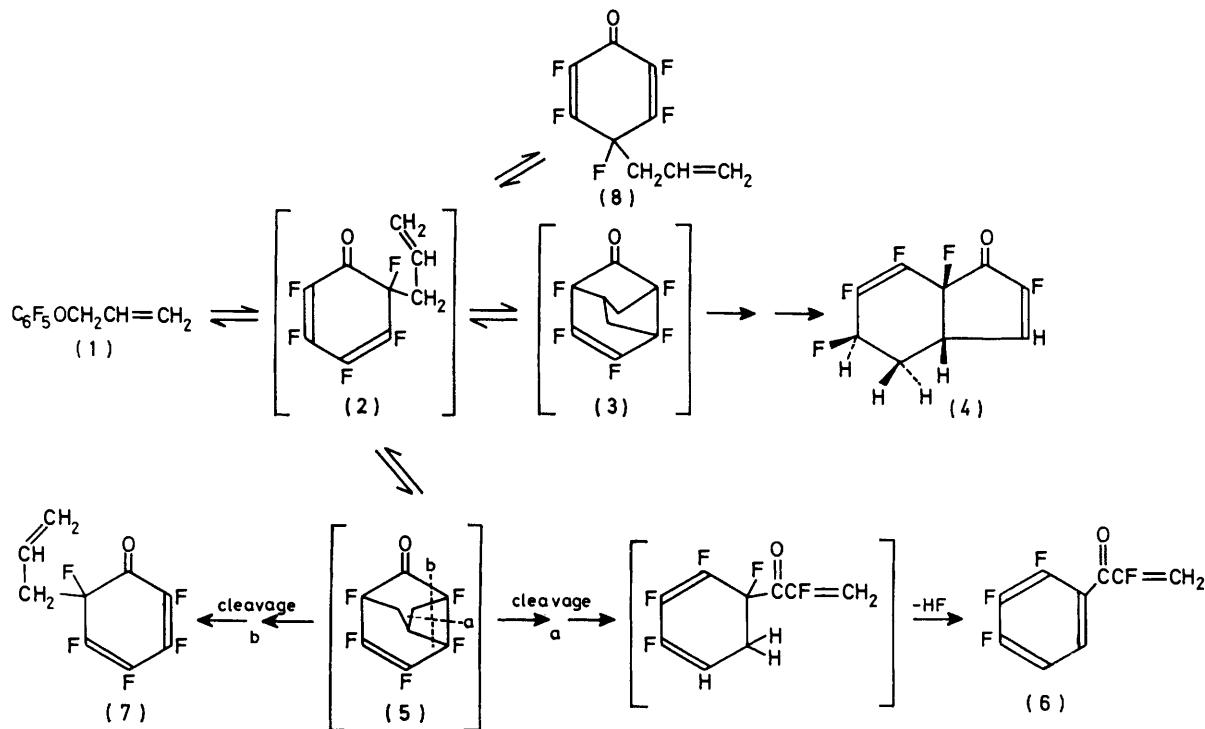
⁶ H. J. Hansen and H. Schmid, *Chem. in Brit.*, 1969, 5, 111.

⁷ G. M. Brooke, *Tetrahedron Letters*, 1971, 2377.

⁸ H. M. M. Shearer; a complete account of the X-ray data will be given in a subsequent publication.

strongly with F-7 and -1, respectively (J 18.0 Hz), were assigned the *exo*-configuration since the relevant dihedral angle from the crystallographic study was 33° ,

more readily than the stepwise rupture of two bonds in a cyclobutane ring, leading to the 2,3,4,5,6-pentafluoro-6-([2,3,3- $^2\text{H}_3$]prop-2-enyl)cyclohexa-2,4-dienone—the



SCHEME 1

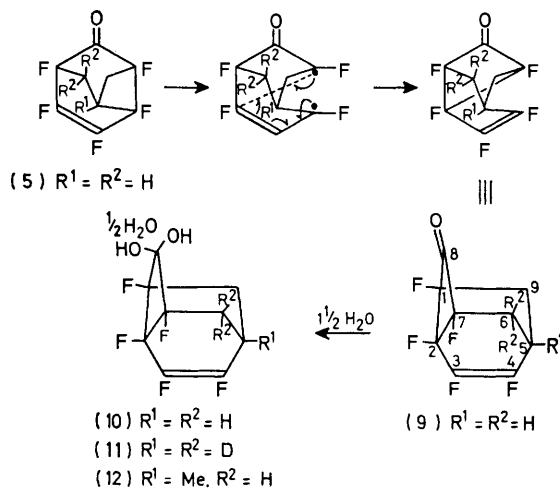
compared with 87° for the *endo*-protons, and it is known that $J_{\text{H,F}}$ decreases when the dihedral angle between the coupling nuclei increases.⁹

The formation of this symmetrical molecule (10) can be rationalised in terms of an overall [1,3] sigmatropic shift occurring in a stepwise manner from the Diels-Alder adduct (5), followed by hydration of the resulting ketone (9) (Scheme 2). A driving force for this reaction could be the formation of conjugated diradicals in the intermediate. In keeping with this proposed mechanism, the thermolysis of pentafluorophenyl[2,3,3- $^2\text{H}_3$]prop-2-enyl ether, under similar conditions to those used for (1), and work up as before, gave a compound the spectroscopic properties of which were entirely consistent with its being racemic 1,2,3,4,7-pentafluoro[5,6,6- $^2\text{H}_3$]tricyclo[3.3.1.0^{2,7}]non-3-ene-8,8-diol hemihydrate (11), in which 43% of the bridgehead deuterium at C-5 had exchanged with hydrogen. The acidity at C-5 could be due in part to the inductive or field effect of the fluorine at C-2.¹⁰

Examination of the volatile residues from the thermolysis of pentafluorophenyl [2,3,3- $^2\text{H}_3$]prop-2-enyl ether by ^1H n.m.r. showed that *ca.* 12% *ortho-ortho* isomerisation had occurred. Though this process does not affect the identity of the product, the low extent of the reaction shows that the retro-Diels-Alder reaction does occur

⁹ K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *J. Amer. Chem. Soc.*, 1966, **88**, 5678.

precursor to the rearranged ether and the cyclohexa-2,5-dienone.



SCHEME 2

The thermolysis of pentafluorophenyl 2-methylbut-2-enyl ether³ at 160°C for 15 days gave a low yield of racemic

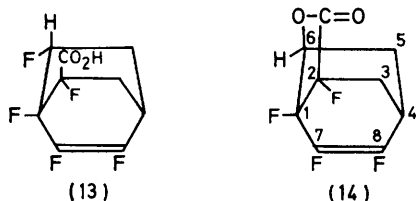
1,2,3,4,7-pentafluoro-5-methyltricyclo[3.3.1.0^{2,7}]non-3-ene-8,8-diol hemihydrate (12), readily

¹⁰ A. Streitwieser and D. Holz, *J. Amer. Chem. Soc.*, 1967, **89**, 692; A. Streitwieser, A. P. Marchand, and A. H. Pudjaatmaka, *ibid.* p. 693.

identified from spectroscopic data by analogy with compound (10).

Dehydration of (10) with phosphorus pentoxide gave the ketone (9), which rapidly picked up moisture from the atmosphere and had to be handled under dry nitrogen. Numerous other examples of solvated *gem*-diols have been reported.¹¹

Reaction of (10) with potassium hydroxide effected rupture of the four-membered ring by a halogenoform-type reaction to give (13), which was readily identified



by spectroscopic methods; the characteristically large $J_{gem-H,F}$ value (56.0 Hz) was readily recognised in the 1H and ^{19}F n.m.r. spectra.

An attempt to decarboxylate the carboxylic acid (13) with 1 equiv. of KOH in water at elevated temperature gave the lactone (14), resulting from a transannular displacement of fluorine by the ideally situated $-CO_2^-$ group.

EXPERIMENTAL

Thermolysis of Pentafluorophenyl Prop-2-enyl Ether (1).—The ether (1) (2.72 g) was sealed in a 10 l flask *in vacuo* and heated at 137–141 °C for 13 days. The products were condensed into a side arm cooled with liquid air, and washed from the vessel with ether; water (1 ml) was added and the solution dried ($MgSO_4$) and evaporated. The residue was evaporated *in vacuo* at room temperature, the vapours passing a water-cooled finger and into a trap cooled in liquid air, to give a mixture of unchanged ether (1) and 2,3,4,5,6-pentafluoro-4-(prop-2-enyl)cyclohexa-2,5-dienone (8) (0.87 g) in the ratio 2 : 1 (by 1H n.m.r.); an unidentified solid (0.51 g) sublimed onto the cold finger. The residue (0.81 g) was sublimed at 60° and 0.001 mmHg and recrystallised from water to give 1,2,3,4,7-pentafluorotricyclo[3.3.1.0^{2,7}]non-3-ene-8,8-diol hemihydrate (10), m.p. 117–118° [Found: C, 43.1; H, 3.4%; M (average), 257 ± 8 (by vapour phase osmometry); m/e , 224. $C_9H_7F_5O_2 \cdot \frac{1}{2}H_2O$ requires C, 43.1; H, 3.2%; $M - \frac{1}{2}H_2O$, 224]; δ_F [(CD_3)₂CO] 140.6 (F-4), 164.5 (F-3), 193.5 (F-1 and F-7), and 218.0 p.p.m. (F-2) upfield from external $CFCl_3$ [J (F-4,H-5) 14.0; J (F-1,H-9-*exo* and F-7,H-6-*exo*) 18.0; J (F-1,H-9-*endo* and F-7,H-6-*endo*) 5.0; J (F-1,F-2 and F-7,F-2) 5.0 Hz]; τ 6.13 (H-5), 7.40 (H-6-*endo* and H-9-*endo*), 8.40 (H-6-*exo* and H-9-*exo*), and 4.58 [C-8(OH)₂ plus $\frac{1}{2}H_2O$ ($W_{\frac{1}{2}}$ 120 Hz)] [J (H-6-*exo*,H-6-*endo* and H-9-*exo*,H-9-*endo*) 12.0 Hz]; ν_{max} 3 550, 3 480, and 3 350 (O-H region), and 1 758 cm^{-1} (CF=CF).

Thermolysis of Pentafluorophenyl [2,3,3- 2H_3]Prop-2-enyl Ether.—The ether (0.55 g) was heated *in vacuo* for 11.7 days at 142–143 °C and the product worked up as above to give three fractions: (i) a mixture (0.30 g) containing unchanged

ether, 2,3,4,5,6-pentafluoro-4-([2,3,3- 2H_3]prop-2-enyl)cyclohexa-2,5-dienone, the rearranged ether pentafluorophenyl [1,1,2- 2H_3]prop-2-enyl ether, and the rearranged 2,3,4,5,6-pentafluoro-4-([1,1,2- 2H_3]prop-2-enyl)cyclohexa-2,5-dienone in the ratio 53 : 35 : 7 : 5, respectively (by 1H n.m.r.); (ii) a volatile sublimate (0.02 g) which was not examined; and (iii) a solid residue (0.23 g) which was recrystallised from water to give 1,2,3,4,7-pentafluoro-[5,6,6- 2H_3]tricyclo[3.3.1.0^{2,7}]non-3-ene-8,8-diol hemihydrate (11), m.p. 115–118° (Found: m/e , 227. $C_9H_4D_3F_5O_2 \cdot \frac{1}{2}H_2O - \frac{1}{2}H_2O$ requires M , 227); δ_F [(CD_3)₂CO] 139.6 (F-4), 162.7 (F-3), 192.4 (F-1), 192.6 (F-7), and 217.0 p.p.m. (F-2) upfield from internal $CFCl_3$ [J (F-1,H-9-*exo*) 18.5 Hz]; τ [(CD_3)₂CO] 7.28 (H-9-*endo*), 8.32 (H-9-*exo*), 3.62 and 3.84 [C-8(OH)₂], and 6.8 ($\frac{1}{2}H_2O + 43\%$ H-5)] [J (H-9-*exo*,H-9-*endo*) 12.0, J (H-9-*endo*,F-1) 4.5 Hz]; ν_{max} 3 530, 3 380, and 3 250 (O-H region), 2 950 (sat. C-H), 2 200 (sat. C-D), and 1 752 cm^{-1} (CF=CF).

Thermolysis of Pentafluorophenyl 2-Methylprop-2-enyl Ether.—The ether (2.48 g) was heated *in vacuo* for 15 days at 160 °C and the complex mixture was worked up as before to give 1,2,3,4,7-pentafluoro-5-methyltricyclo[3.3.1.0^{2,7}]non-3-ene-8,8-diol hemihydrate (12) (0.10 g), m.p. 112–113° (Found: C, 45.4; H, 4.2%; m/e , 238. $C_{10}H_9F_5O_2 \cdot \frac{1}{2}H_2O$ requires C, 45.3; H, 4.2%; $M - \frac{1}{2}H_2O$, 238); δ_F [(CD_3)₂CO] 155.7 (F-4), 163.4 (F-3), 192.4 (F-1 and -7), and 215.6 p.p.m. (F-2) upfield from external $CFCl_3$ [J (F-1,H-9-*exo* and F-7,H-6-*exo*) 18.0, J (F-1,F-2 and F-7,F-2) 5.0, J (F-2,F-4) 8.0 Hz]; τ [(CD_3)₂CO] 3.80 [C-8(OH)₂], 6.63($\frac{1}{2}H_2O$), 7.50 (H-6-*endo* and H-9-*endo*), 8.35 (H-6-*exo* and H-9-*exo*), and 8.62 (CH₃-5)] [J (H-6-*exo*,H-6-*endo* and H-9-*exo*,H-9-*endo*) 12.0 Hz]; ν_{max} 3 580, 3 420, and 3 190 (O-H region), and 1 748 cm^{-1} (CF=CF).

1,2,3,4,7-Pentafluorotricyclo[3.3.1.0^{2,7}]non-3-en-8-one (9).—The diol hemihydrate (10) (0.10 g) and P_2O_5 (0.33 g) were sublimed at 40° and 0.01–0.05 mmHg and the product handled under dry N_2 to give the ketone (9) (0.09 g), m.p. 84–86° (Found: C, 48.0; H, 2.1%; M^+ , 224. $C_9H_5F_5O$ requires C, 48.2; H, 2.2%; M , 224); δ_F ($CDCl_3$) 131.7 (F-4), 161.0 (F-3), 186.6 (F-7 and -1), and 216.1 p.p.m. (F-2) upfield from external $CFCl_3$ [J (F-1,H-9-*exo* and F-7,H-6-*exo*) 15.0 Hz]; τ ($CDCl_3$) 6.63 (H-5), 6.93 (H-6-*endo* and H-9-*endo*), and 7.54 (H-6-*exo* and H-9-*exo*) [J (H-6-*exo*,H-6-*endo* and H-9-*exo*,H-9-*endo*) 14.0 Hz]; ν_{max} 1 840 (C=O) and 1 760 cm^{-1} (CF=CF).

1,2-*exo*,6-*exo*-7,8-Pentafluorobicyclo[2.2.2]oct-7-ene-2-endo-carboxylic Acid (13).—The diol hemihydrate (10) (1.28 g) and potassium hydroxide (27 ml; 0.61M) were boiled together for 3 min; the solution was acidified with hydrochloric acid (2M) and then extracted with ether. The dried ($MgSO_4$) extracts were evaporated to give the acid (13) (0.96 g), m.p. 147–148° (from benzene) (Found: C, 44.4; H, 3.2%; M^+ , 242. $C_9H_7F_5O_2$ requires C, 44.4; H, 3.2%; M , 242); δ_F [(CD_3)₂CO] 141.4 (F-8), 155.8 (F-2), 158.6 (F-7), 184.4 (F-6), and 204.6 p.p.m. (F-1) upfield from external $CFCl_3$ [J (F-6,H-6) 56.0, J (F-6,F-2) 37.5, J (F-6-*exo*,H-5-*exo*) 20.0, J (F-6-*exo*,H-5-*endo*) 13.0, J (F-8,H-4) 16.0 Hz]; τ [(CD_3)₂CO] 4.62 (H-6-*endo*), 6.87 (H-4), and 7.18–8.85 (complex, H-5-*exo*, H-5-*endo*, H-3-*exo*, H-3-*endo*); ν_{max} 1 750 (CF=CF) and 1 715 cm^{-1} (C=O).

1,2,7,8-Tetrafluorobicyclo[2.2.2]oct-7-ene-2,6-carbolactone (14).—The acid (13) (0.24 g) and 1 equiv. of potassium hydroxide (3.35 ml; 0.296M) were heated together in a sealed tube at 160 °C for 19 h. The mixture was extracted with ether, the extracts were dried ($MgSO_4$) and evaporated,

¹¹ W. J. Middleton and R. V. Lindsey, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 4948; E. M. Schulman, O. D. Benner, D. R. Schulman, and F. M. Laskovics, *ibid.*, 1976, **98**, 3793.

and the residue was sublimed at 40° and 0.001 mmHg to give the lactone (14) (0.07 g), m.p. 149—150° (from toluene) (Found: C, 48.4; H, 2.6%; M^+ , 222. $C_9H_8F_4O_2$ requires C, 48.7; H, 2.78%; M , 222); δ_F [(CD_3)₂CO] 135.5 (F-8), 161.3 (F-7), 184.7 (F-2), and 205.1 p.p.m. (F-1) upfield from internal $CFCl_3$ [J (F-8,H-4) 16.0, J (F-2,H-3-*exo*) 27.0 Hz]; τ 4.75 (H-6), 6.68 (H-4), and 6.99—8.00 (complex incor-

porating H-5-*exo*, H-5-*endo*, H-3-*exo*, and H-3-*endo*); ν_{max} . 1 808 (C=O) and 1 755 cm^{-1} (CF=CF).

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