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2,3,4,5,7-PENTAFLUOROTRICYCLO(3.3.1.O^{2,7}) NON-3-EN-6-ONE, AN INTERNAL DIELS-ALDER ADDUCT FROM THE CLAISEN REARRANGEMENT INTERMEDIATE FROM PENTAFLUOROPHENYL PROP-2-ENYL ETHER

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SUMMARY

The title compound (3), the first carbocyclic Diels-Alder adduct to be isolated from the Claisen rearrangement intermediate from the thermolysis of an aryl prop-2-enyl ether, has been characterised from its spectroscopic data and by its conversion to 1,2,3,4,7-pentafluorotricyclo[3.3.1.O^{2,7}]non-3-en-8,8 diol hemihydrate (5).

In an earlier paper [1] we described the thermolysis of pentafluorophenyl prop-2-enyl ether (1) in the vapour phase at 137 - 141° for 13 days and identified among the products 1,2,3,4,7-pentafluorotricyclo[3.3.1.O^{2,7}]non-3-en-8,8-diol hemihydrate (5) (30%). The formation of (5) was rationalised in terms of a stepwise [1,3-]sigmatropic rearrangement of the intermediate Diels-Alder adduct (3) produced from the Claisen rearrangement intermediate (2), and hydration of the product (4) (Scheme 1). Also present in the reaction mixture was another compound (X) isomeric with (1) and (4) which we have now identified as the Diels-Alder intermediate, 2,3,4,5,7-pentafluorotricyclo[3.3.1.O^{2,7}]non-3-en-6-one (3) (19%) on the basis of one chemical transformation and the comparison of its spectroscopic data with those of closely related compounds. The alternative Diels-Alder adduct (6) is involved in the formation of other products from (1) but only at considerably higher reaction temperatures (440 - 480°) [2].

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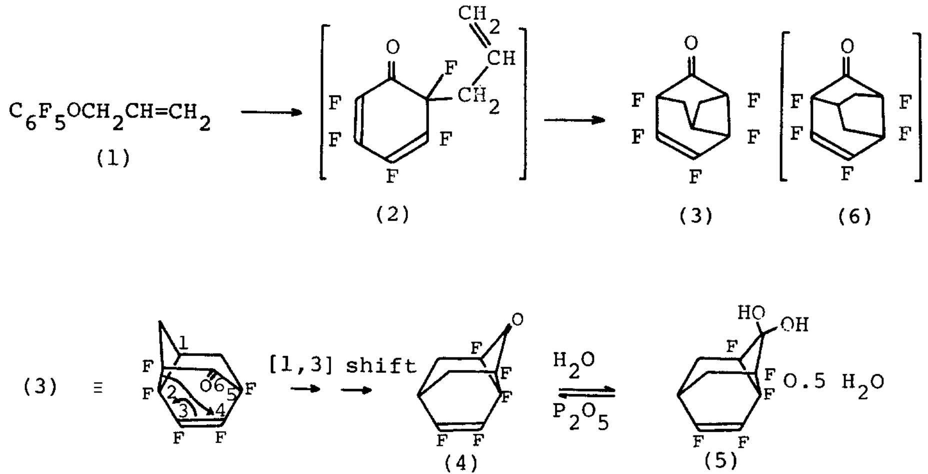
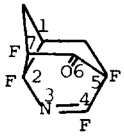


Scheme 1

The thermolysis of the previously unidentified compound (X) in the vapour phase at 140° for 8.7 days and work-up of the product as described previously [1] gave (5) (31%), the formation of which is entirely consistent with (X) being the Diels-Alder adduct (3).

Since our earlier publication [1] we have described the preparation of authentic analogues of (3), namely the tetrafluoroazatricyclo$[3.3.1.0^{2,7}]$non-3-en-6-ones (7) and (8) by the thermolyses of 2,3,5,6-tetrafluoro-4-pyridyl and 2,4,5,6-tetrafluoro-3-pyridyl prop-2-enyl ethers respectively [3]. The benzo-analogue (9) has also been obtained from the photolysis of 1,3,4,5,6,7,8-heptafluoro-1-(prop-2-enyl)naphthalen-2-one [4]. The spectral data for (3) are entirely consistent with those of (7), (8) and (9). Thus, the characteristic C=O absorptions in the i.r. spectra measured in nujol were all at 1778 cm.$^{-1}$ The chemical shifts in the ^{19}F n.m.r. spectra are shown in the Table. In this Table, the assignments for F-3 and F-4 in (3) give the more equal values for the effect of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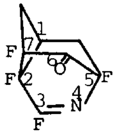
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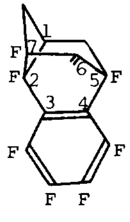
(9)

nitrogen on the adjacent vinylic C-F in (7) and (8) (downfield shifts of 94.3 and 94.0 p.p.m. respectively). The shifts of the fluorine at F-7 remain essentially unchanged throughout the series, while the nitrogen shifts the adjacent bridgehead fluorine 48.9 p.p.m. downfield for F-2 in (7) (212.4 - 163.5 p.p.m.), and 45.5 p.p.m. downfield for F-5 in (8) (193.2 - 147.7 p.p.m.). In the benzo-analogue (9) the bridgehead fluorines are shifted downfield (13.9 p.p.m. for F-2 and 8.4 p.p.m. for F-3).

TABLE

Chemical shifts in $(CD_3)_2CO$ upfield from $CFCl_3$ as internal standard

Compound	F-2	F-3	F-4	F-5	F-7
(7)	163.5	-	61.5	192.2	176.2
(8)	203.8	57.4	-	147.7	175.9
(9)	198.5	-	-	184.8	173.5
(3)*	212.4	151.4	155.8	193.2	175.7

* These shifts were upfield from external $CFCl_3$

It is noteworthy that the first internal Diels-Alder intermediate to be isolated from a Claisen rearrangement reaction utilised 2,6-dimethylphenyl prop-2-ynyl ether [5]. Compound (3) described in this paper is the first internal Diels-Alder adduct to be characterised from a Claisen rearrangement reaction involving an aryl prop-2-enyl ether.

EXPERIMENTAL

Thermolysis of pentafluorophenyl prop-2-enyl ether (1)

The thermolysis of the ether (1) (2.72 g) in the vapour phase at 137 - 141° for 13 days gave in addition to the products described previously [1], 2,3,4,5,7-pentafluorotricyclo[3.3.1.$0^{2,7}$]non-3-en-6-one (3) (0.51 g), m.p. 93.5 - 94°C [from toluene-petroleum ether (b.p. 80 - 100°)] (Found:

C, 48.2; H, 2.0; M^+, 224. $C_9H_5F_5O$ requires C, 48.2; H, 2.2%; M^+, 224; δ_F [$(CD_3)_2CO$] 151.4 (F-3), 155.8 (F-4), 175.7 (F-7), 193.2 (F-5) and 212.4 p.p.m. (F-2) upfield from external $CFCl_3$; δ_H [$(CD_3)_2CO$] 2.35 (multiplet), 2.55 (multiplet) and 3.28 (multiplet) in the ratio 1:2:2 respectively; υ_{max} 1748 (CF=CF) and 1778 cm.$^{-1}$ (C=O).

Thermolysis of 2,3,4,5,7-Pentafluorotricyclo[3.3.1.$0^{2,7}$]non-3-en-6-one (3)

The internal Diels-Alder adduct (3) (0.478 g) was sealed in a 2 l. flask in vacuo and heated at 140° for 8.7 days. The flask was washed out with ether, the ether evaporated and the residue crystallised from water to give 1,2,3,4,7-pentafluorotricyclo[3.3.1.$0^{2,7}$]non-3-en-8,8-diol hemihydrate (5) (0.167 g) [1].

ACKNOWLEDGEMENT

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