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Valence-bond Isomer Chemistry. Part 11 [1]. Thermal Rearrangement of the Diels-Alder Adduct of Hexafluorobicyclo-[2.2.0]hexa-2,5-diene and 2,3-Dimethylbuta-1,3-diene: a [1,3] Sigmatropic Shift of Fluorine

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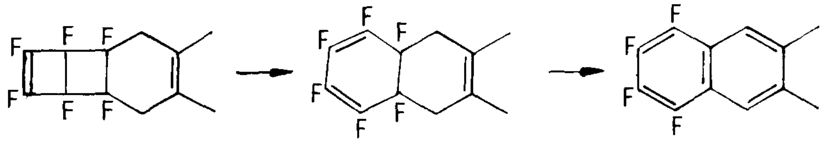
SUMMARY

Flow pyrolysis of the Diels-Alder adduct of hexafluorobicyclo[2.2.0]hexa-2,5-diene and 2,3-dimethylbutadiene gives an unusual product, the Diels-Alder adduct of hexafluorobenzene and 2,3-dimethylbuta-1,3-diene, and thence via an exclusive [1,3] sigmatropic fluorine shift, its isomeric triene. Loss of hydrogen fluoride from the unusual Diels-Alder adduct readily affords 1,2,3,4-tetrafluoro-6,7-dimethylnaphthalene.

DISCUSSION

Hexafluorobicyclo[2.2.0]hexa-2,5-diene is a reactive dienophile in the Diels-Alder reaction, forming 1:1- and 1:2-adducts with a number of dienes [2]. We here describe a study of the thermal rearrangement of the 2,3-dimethylbuta-1,3-diene adduct (1).

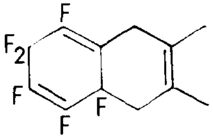
This adduct (1), when heated at 160 °C for 5 days, produced 1,2,3,4-tetrafluoro-6,7-dimethylnaphthalene (2) in reasonable yield (65%). The reaction presumably involved formation of the tetralin (3), which aromatized by loss of hydrogen fluoride.



(1) (3) (2)

Triene(3) is a rare type of compound, the Diels-Alder adduct of an aromatic compound (hexafluorobenzene) and a diene (2,3-dimethylbuta-1,3-diene), *and might have been expected to undergo easy retro-reaction.* In an attempt to obtain (3), flow pyrolysis of (1) was investigated. At 500 °C with the briefest of contact times (ca. 200 μs), a rather unstable product, particularly in the absence of a little solid sodium carbonate, was obtained, which was shown spectroscopically to comprise triene (3) (92%), together with the isomeric triene (4) (8%).

(1) $\xrightarrow{500\ ^{\circ}C}$ (3) +



(4)

The product rapidly darkened at room temperature, producing mainly the naphthalene (2). With longer contact times, triene (4) was the major product. For example, at 425 °C with a contact time of ca. 40 ms, the product comprised the compounds (1), (2), (3) and (4), in the ratio 2:6:7:85.

For thermal reactions, both [1,3] and [1,5] sigmatropic fluorine shifts are allowed processes [3], and it is interesting that, in the conversion of (3) into (4), the *product of a [1,3] shift is obtained exclusively.* Only a few apparent thermal sigmatropic shifts of fluorine have been reported [4], and it appears that for six-membered ring systems, [1,3] shifts are preferred.

Thermal Reactions of 1,2,3,4,5,6-Hexafluoro-8,9-dimethyltricyclo[4.4.0.0.^{2,5}]-deca-3,8-diene [2]

(a) At 160 °C

The above tricyclodecadiene (0.20 g, 0.75 mmol) was sealed in a Pyrex ampoule (10 cm^3) and heated at 160 °C for 5 days. The ampoule was then opened (acidic fumes evolved), and the product was extracted with chloroform and sublimed at 75 °C and 0.01 mmHg to give 1,2,3,4-tetrafluoro-6,7-dimethylnaphthalene (0.11 g, 0.48 mmol, 65%) (Found: C, 63.2; H, 3.5; F, 33.8%, $M^{+\bullet}$, 228. Calc for $C_{12}H_8F_4$: C, 63.2; H, 3.5; F, 33.3%, M, 228), as a white solid, m.p. 103-4 °C (lit. [5] 103-4 °C) with δ_H (in $CDCl_3$) 7.6 (H) and 2.35 (CH_3), and δ_F (external CF_3CO_2H) -77.0 and -86.5 p.p.m. (AA'BB'-type spectrum), and spectroscopic properties similar to those reported [6].

(b) Flow Reaction

The tricyclodecadiene (0.50 g, 1.9 mmol) was heated to 65 °C *in vacuo* and its vapour at *ca*. 0.005 mmHg passed through a silica tube (heated length 40 cm x 1.2 cm i.d.) heated to 500 °C during 90 s (estimated contact time *ca*. 200μs). The products (0.49 g, 98% recovery) were collected at -196 °C in a trap containing solid sodium carbonate (50 mg), and immediate examination by ^{19}F n.m.r. spectroscopy indicated them to be a 92:8 mixture of 1,2,3,4,5,6-hexafluoro-8,9-dimethylbicyclo[4.4.0]deca-2,4,8-triene and 2,3,3,4,5,6-hexafluoro-8,9-dimethylbicyclo[4.4.0]deca-1,4,8-triene (Found: *M*$^{+\bullet}$, 268.0686. Calc. for $C_{12}H_{10}F_6$: *M*, 268.0686), as a colourless liquid at room temperature.

The tricyclodecadiene (0.40 g, 1.50 mmol), heated to 35 °C, was similarly passed through the silica tube at 425 °C and *ca*. 0.04 mmHg over 25 min. (contact time *ca*. 40 ms). The products (0.38 g, 95% recovery) were collected in a trap cooled to -196 °C, and g.l.c. analysis (1.5 m SE 30 column at 130 °C) indicated the composition: recovered tricyclodecadiene (2%),the deca-2,4,8-triene (7%), the deca-1,4,8-triene (85%), and 1,2,3,4-tetrafluoro-6,7-dimethylnaphthalene (6%).

The major component (nc) was obtained pure with difficulty and miserable recovery (6%) by preparative scale g.l.c. (10 m SE 30 column at 160 °C) (Found: *M*$^{+\bullet}$, 268.0686. $C_{12}H_{10}F_6$ requires *M*, 268.0686), as a white solid, m.p. 45-6 °C, with $\nu_{max.}$ 1770 (CF=CF str.) and 1721 cm^{-1} (CF=CR str.) (*cf*., 1-methylheptafluorocyclohexa-1,4-diene with $\nu_{max.}$ 1780 and 1734 cm^{-1} [7]). δ_F -30.3 (F-3), -62.7 (F-2), -70.0 (F-5), -79.0 (F-4), and -86-3 p.p.m. (F-6). This assignment of chemical shifts was based upon the reported values for 3-methylheptafluorocyclohexa-1,4-diene and 1-methylheptafluorocyclohexa-1,3-diene [7], and the shift of the CF_2 absorption (F-3) was particularly indicative of a 1,4-diene.

The triene (3) [containing 8% of (4)] showed δ_H 1.47 (CH_3) and 2.46 (CH_2) and δ_F -77.0 (F-3,4), -81.8 (F-2,5), and -96.3 p.p.m. (F-1,6), the olefinic fluorine shifts being similar to those of perfluorocyclohexa-1,3-diene [7] .

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