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DIELS-ALDER REACTIONS OF POLYFLUOROCYCLOHEXA-1,3-DIENES. PART VIII [1]. REACTION OF TRIFLUOROACETONITRILE WITH PERFLUOROTRICYCLO[6,2,2,$0^{2,7}$]DODECA-2,6,9-TRIENE. A SYNTHESIS OF PERFLUORO-3-METHYLISOQUINOLINE

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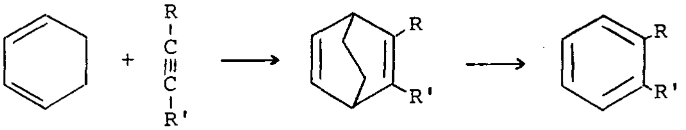
SUMMARY

The Diels-Alder reaction between perfluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6,9-triene (1) and trifluoroacetonitrile provides a route to perfluoro-3-methylisoquinoline (5) and perfluoro-9-aza-10-methyltricyclo[6,2,2,$0^{2,7}$]dodeca-2,4,6,9-tetraene (3) which yields (5) on pyrolysis. Perfluorobenzobicyclo[2,2,2]oct-2-ene (4) is formed as a biproduct resulting from the initial Diels-Alder addition between (1) and tetrafluoroethylene.

INTRODUCTION

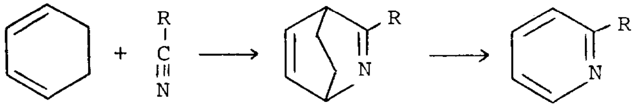
In earlier papers in this series we reported that the $-CF_2CF_2-$ bridge in the Diels-Alder adducts of alkynes with polyfluorocyclohexa-1,3-dienes was eliminated on flash-vacuum pyrolysis, providing a route to fluorinated benzenes with specific substitution patterns (Scheme 1) [2,3]. This process was successfully extended to the synthesis of 2-substituted



(unmarked bonds to fluorine)

Scheme 1

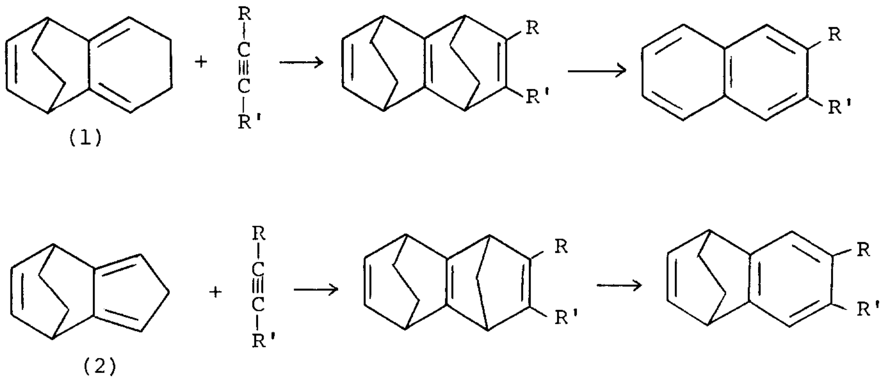
tetrafluoropyridines by use of nitriles as dienophiles, and in this work primary Diels-Alder adducts of nitriles with 1,3-dienes were isolated for the first time (Scheme 2) [4].



(unmarked bonds to fluorine)

Scheme 2

Subsequently the syntheses of 2,3-disubstituted hexafluoronaphthalenes, polyfluorobenzobicyclo[2,2,2]octa-2,5-dienes and related compounds from perfluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6,9-triene (1) and perfluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene (2) were also established (Scheme 3) [1,5].

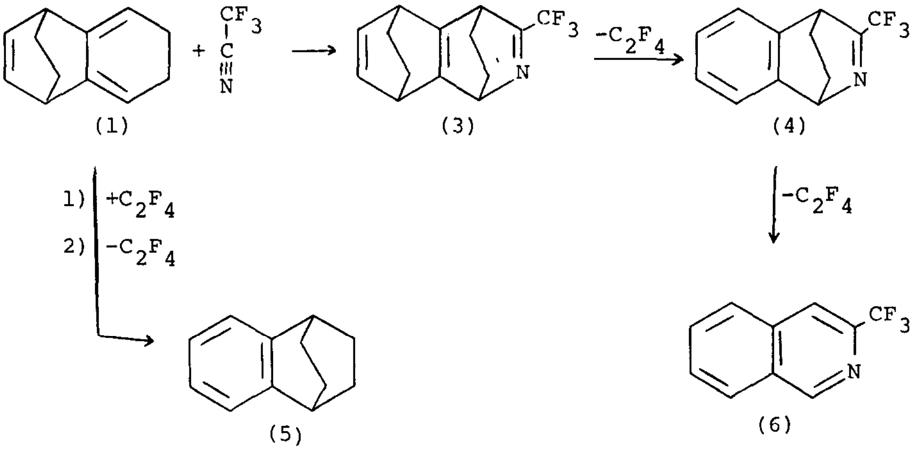


(unmarked bonds to fluorine)

Scheme. 3

RESULTS AND DISCUSSION

The reaction of nitriles with fluorinated dienes requires temperatures in the region of 350 to 400° consequently only inherently thermally stable nitriles can be used. We first attempted to extend the series of syntheses of fluorinated aromatic compounds outlined above to the polyfluoroisoquinolines by reaction of nitriles with triene (2) since it is more readily accessible than (1), however this was unsuccessful since under the forcing conditions required to effect reaction extensive decomposition occurred and g.l.c. analysis of the product indicated a very complex mixture [6]; this attempt was abandoned. However, triene (1) on heating with trifluoroacetonitrile gave a 30.5% yield (38% before separation and purification) of perfluoro-3-methylisoquinoline (6), 11.5% (17% before separation) of perfluoro-9-aza-10-methyltricyclo[6,2,2,$0^{2,7}$]dodeca-2,4,6,9-tetraene (4), perfluorobenzobicyclo[2,2,2]oct-2-ene (5) (1.5%), and mass spectroscopic evidence for traces of the primary Diels-Alder adduct (3) (Scheme 4). The reaction was carried out by



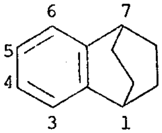
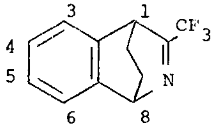
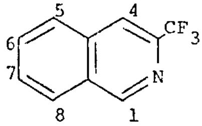
Scheme 4

heating triene (1) with a large excess of trifluoroacetonitrile in Pyrex ampoule at 400°. The excess of trifluoroacetonitrile was used in an attempt to maintain high pressures throughout the course of the reaction and so minimise the elimination of $-CF_2CF_2-$ bridges from the primary adduct (3), this objective was not achieved and the only evidence for compounds of structure (3) was a peak in the mass spectrum at m/e 505 corresponding to the molecular ion for

(3); nevertheless the product mixture before separation contained 55% of products derived from initial Diels-Alder addition. The primary adduct (3) eliminated the $-CF_2CF_2-$ bridge of the carbocyclic system to give (4), there was no evidence for the isomeric structure which would have arisen if the $-CF_2CF_2-$ bridge in the heterocyclic system had been eliminated. The structure of (4) was assigned on the basis of its mass spectrum which showed the expected molecular ion at m/e 405 (19%) and a consistent fragmentation pattern, in particular a base peak at m/e 305 arising from elimination of C_2F_4 from the molecular ion, an observation which was parallelled in the pyrolysis of (4) to give (6); the i.r. and u.v. were consistent with the assigned structure, elemental analysis for fluorine supported the assigned formula, but as with some other fluorocarbon molecules difficulties in obtaining complete combustion resulted in low carbon and high nitrogen values. The ^{19}F n.m.r. spectrum (Table) completes the assignment of (4); the bridging $-CF_2CF_2-$ unit appearing as a pair of overlapping AB systems; the two tertiary fluorines can be assigned since the one adjacent to nitrogen experiences a large dowfield shift; extensive long range coupling with the bridging $-CF_2CF_2-$ and $-CF_3$ units gives essentially unresolved broad signals however the expected large coupling between the tertiary fluorines and the 'peri' aromatic fluorines can only be accommodated in one of the aromatic resonances thus confirming the assignments based initially on shifts. The structural assignment of (6) was based on the mass, i.r. and u.v. spectra, together with satisfactory elemental analysis for fluorine. The ^{19}F n.m.r. of (6) (Table) completes the assignment, being completely consistent with the trends established in studies of a number of fluorinated isoquinolines synthesised in this department [7], the salient features being the large downfield shift experienced by the fluorine on the carbon adjacent to nitrogen (C_1) and the large peri (1,8 and 4,5) and para (1,4) coupling constants. Most of the resonances in the spectrum were not well resolved due to extensive long range coupling with the $-CF_3$ group so only the large clearly distinguishable couplings have been recorded.

TABLE

^{19}F N.m.r. Spectral Parameters[a]

Compound[b]	-C-F	$-CF_2CF_2-$ $-CF_3$	Aromatic F
 (5)	at C_1 and C_7 219.6(2) $J_{1,3(6,7)}$ 38	δ_A 125.3(4)[c] δ_B 127.6(4) J_{AB} 250	at C_3 and C_6 145.0(2) at C_4 and C_5 147.9(2)
 (4)	at C_1 213.2(1) at C_8 173.1(1)	δ_A 125.0(1) δ_B 129.4(1) J_{AB} 230 δ'_A 126.2(1) δ'_B 127.7(1) $J_{A'B'}$ 235 CF_3 73.9(3)	at C_3 and C_6 145.8(2) at C_4 and C_5 151.3(2)
 (6)		CF_3 66.3(3)	at C_6 and C_7 148.5(1) 145.7(1) at C_4 132.6(1) at C_5 143.3(1) $J_{4,5}$ 60 at C_1 61.2(1) at C_8 134.4(1) $J_{1,8}$ 66, $J_{1,4}$ 30

[a] Shifts are in p.p.m. w.r.t. internal $CFCl_3$; integrated intensities in parenthesis; coupling constants in Hz.

[b] Unmarked valences to fluorine atoms, (4) in d_6 acetone solution, (3) and (5) as neat liquids.

[c] Pseudo AB quartet.

The assignment of structure for compound (5) was based primarily upon the ^{19}F n.m.r. data (Table). The $-CF_2CF_2-$ bridges are equivalent and appear as a pseudo AB system (J_{AB} 250 Hz), the tertiary and aromatic fluorines are readily assigned on the basis of chemical shift, and the aromatic fluorines at C_3 and C_6 identified by the large 'peri' coupling (38 Hz) between them and the tertiary fluorines (although this coupling is only clearly resolved in the aromatic fluorine resonances, the tertiary resonances being essentially unresolved broad bands). The i.r., u.v. and mass spectra of (5) supported the assigned structure, showing absorptions typical for the fluorinated aromatic ring and the correct molecular ion respectively. Compound (5) must have arisen as a result of Diels-Alder addition of tetrafluoroethylene (produced *in situ* from the pyrolysis of compounds (3) and (4)) to the triene (1) followed by the expulsion of the $-CF_2CF_2-$ bridge already present to give the aromatic ring. Formation of (5) from (1) by an isomerization pathway can be ruled out since studies of the thermal reactions (1) show that although thermal isomerizations can occur they do not happen under the experimental conditions used here and when they do occur the product is not (4) [8]. The isolation of (5) therefore represents a rare example of the Diels-Alder addition of tetrafluoroethylene to a fluorinated diene. The observation of 4 + 2 addition in this case, rather the usually preferred 2 + 2 addition [4], probably depends on a combination of enhanced reactivity of triene (1) and steric inhibition of 2 + 2 addition.

EXPERIMENTAL

General.- Techniques and apparatus were as described previously. Perfluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene [1,9] and trifluoroacetonitrile [4] were prepared as described previously.

Diels-Alder Reaction of Perfluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6,9-triene (1) with Trifluoroacetonitrile

Perfluoroacetonitrile (10.9 mmoles) and triene (1) (2.20 g, 5.37 mmoles) were heated at 400° for 14 h in a Pyrex ampoule (35 ml) which had been sealed in vacuo. The mixture was fractionated by conventional vacuum line techniques to give: (i) a gaseous fraction (ca. 15 mmoles) shown by i.r. and mass spectroscopy to be predominantly trifluoroacetonitrile and tetrafluoroethylene; and (ii) a liquid mixture which was separated in two stages by preparative gas chromatography. Chromatography on a silicone oil/chromosorb P (30%) stationary phase at 150° allowed a separation into a liquid mixture and a longer retained solid. Recrystallization of the solid from petroleum (40/60) at -20° gave perfluoro-3-methylisoquinoline (6) (0.51 g, 1.64 mmoles, 30.5%) [Found: F, 55.9%; M (mass spectrometry), 305. $C_{10}NF_9$ requires F, 56.1%; M, 305] white crystals m.p. 30°, υ_{max} 1658, 1628, 1533, 1490 and 1475 cm^{-1}, λ_{max} 268 (ε, 3600)sh, 273 (5100), 283 (4600), 311 (5300), 322 (6600)sh and 325 nm (6900). The liquid mixture was finally separated on a stationary phase of di-n-decylphthalate/chromosorb P at 125° to give: (a) a liquid (ca. 0.01 g), shown by i.r. to be almost pure triene (1) but whose mass spectrum showed ions at m/e 505 consistent with the presence of trace amounts of the Diels-Alder adduct (3) of (1) with trifluoroacetonitrile; (b) perfluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,4,6-triene (perfluorobenzobicyclo[2,2,2]oct-2-ene (5) (0.032 g, 0.08 mmoles, 1.5%) [Found: M (mass spectroscopy), 410. $C_{12}F_{14}$ requires M, 410] m.p. 59°, υ_{max} 1510 cm^{-1} and λ_{max} 267 nm (ε, 1200); (c) perfluoro-9-aza-10-methyltricyclo[6,2,2,$0^{2,7}$]dodeca-2,4,6,9-tetraene (4) (0.25 g, 0.62 mmoles, 11.5%) [Found: F, 61.0%; M (mass spectrometry), 405. $C_{12}NF_{13}$ requires F, 61.0%; M, 405] a colourless liquid, υ_{max} 1510 cm^{-1} and λ_{max} 275 nm (ε, 1400); and (d) perfluoro-1,2-dihydronaphthalene (ca. 0.1 g).

Pyrolysis of Perfluoro-9-aza-10-methyltricyclo[6,2,2,$0^{2,7}$]-dodeca-2,4,6,9-tetraene (4)

Compound (4) (0.051 g, 0.125 mmoles) was pyrolysed by passage through a quartz tube (45 cm. x 1.2 cm. i.d.) at 660° and 10^{-3} mm Hg to give: (i) tetrafluoroethylene (0.12 mmoles) with correct i.r. spectrum; and (ii) perfluoro-3-methylisoquinoline (0.039 g) shown by i.r. spectroscopy and analytical gas chromatography to be contaminated with tetraene (4) (ca. 3%).

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