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HETEROCYCLIC POLYFLUORO-COMPOUNDS. PART 38 [1]. PHOTOCHEMICAL ADDITION OF BUT-2-YNE TO PENTAFLUOROPYRIDINE TO GIVE 1:1 AND 2:1 ADDUCTS

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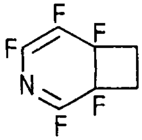
SUMMARY

Pentafluoropyridine adds photochemically to but-2-yne to give two 1:1 adducts, 1,2,4,5,6-pentafluoro-7,8-dimethyl-3-aza- and 1,2,5,6,8-pentafluoro-3,4-dimethyl-7-aza-bicyclo-[4.2.0]octa-2,4,7-triene and a 1:2 adduct, 1,2,5,6,8-pentafluoro-3,4,9,10-tetramethyl-7-azatricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene.

DISCUSSION

Pentafluoropyridine adds photochemically to hydrocarbon olefins to give 1:1 adducts having the 1,2,4,5,6-pentafluoro-3-azabicyclo[4.2.0]octa-2,4-diene skeleton (1) with acyclic olefins [2], and 1:2 adducts having the 1,2,5,6,8-pentafluoro-7-azatricyclo[4.2.2.$0^{2,5}$]dec-7-ene skeleton (2) [2,3].



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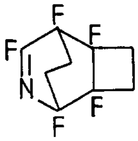

(2)

The reaction with the acetylene, but-2-yne, was investigated to see how it compared.

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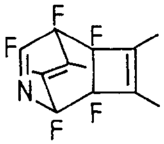
Irradiation of a mixture of pentafluoropyridine and but-2-yne with u.v. light (λ>200 nm) led to a slow conversion into two 1:1 adducts (7 and 2%) and a 1:2 adduct (8%). The structure (3) of the 1:2 adduct appeared analogous to the structure of the olefin adducts. It showed (CCl_4 solution) $\nu_{max.}$ 1709 cm^{-1} (CF=N stretch), δ_F (positive values to low field of trifluoroacetic acid) 12.1 (CF=N [4]), -85.4 (CF-N), -110.2, -119.9, and -125.8 p.p.m. (bridgehead CF), δ_H 1.8 and 1.9p.p.m. (CH_3C=), and a base peak in its mass spectrum



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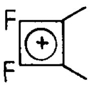

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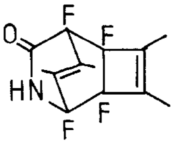
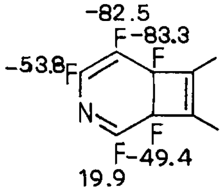


(5)

corresponding to the ion (4) arising <u>via</u> retro-Diels-Alder cleavage. The F-19 n.m.r. absorptions were similar to those of the ethylene 1:2 adduct, but relative to this, were all shifted <u>ca</u>. 10 p.p.m. to high field. The adduct was readily hydrolysed to the amide (5) with δ_F ($CDCl_3$ solution) -101.7 (CF-N), -110.4, -115.7, and -124.3 p.p.m., and δ_H 7.4 (NH), 1.95 and 1.8 p.p.m. (CH_3C=).

More problematic were the structures of the 1:1 adducts, which were difficult to handle, reacting with moist air, and blackening rapidly. The major isomer showed $\nu_{max.}$ 1730, 1680, and 1669 cm^{-1} in the double-bond stretching region. The olefin adducts also show a band around 1730 cm^{-1}, and mono- and bi-cyclic structures were considered. It showed δ_F (resolved coupling constants in parentheses) 19.9 (CF=N, 27, 28 Hz), -49.4 (broad and complex), -53.8 (29, 27, 13, 5 Hz), -82.5 (26, 3, 3 Hz), and -83.3 p.p.m. (28, 10 Hz), and δ_H 1.85 p.p.m. Perfluorocyclo-octatetraene has $\nu_{max.}$ [5] 1724 and 1695 cm^{-1} and δ_F -45.0 p.p.m., and its chemical shift in particular would seem to rule out an azacyclo-octatetraene structure for this adduct. The fine structure of the F-19 absorptions resembled in many ways the fine structure of the absorptions of the olefin 1:1 adducts [2], and these seem clearly bicyclic, since inter alia the adduct from 2-methylpropene shows non-equivalent methyl groups in its H-1 n.m.r. spectrum [2]. The structure (6) thus seems probable, with the assignments of chemical shifts shown, analogous to those of the olefin adducts. The low-field shift of the -49.4 p.p.m. absorption is unexplained; the corresponding absorption in the ethylene adduct has δ_F -71 p.p.m.



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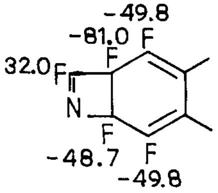
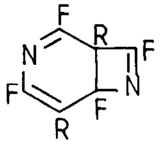


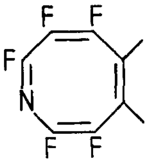
(7)

The minor 1:1 adduct had a mass spectrum very similar to that of the major isomer, showed $\nu_{max.}$ 1770s, 1690s, and 1632m cm^{-1}, the frequency of the first band being noticably higher than that of the olefin adducts, δ_F 32.0 (CF=N), -48.7, -49.8 (2F), and -81.0 p.p.m., and δ_H 2.04 and 2.18 p.p.m. The structure (7) is suggested for the following reasons. The low-field shift of the CF=N absorption resembles that of the corresponding fluorine in compound (8) [6], and the C=N stretching frequency is in accord. Replacement of fluorine by methyl in the CF=CF group results in a substantial low-field shift [7,8] of the absorption of the remaining fluorine, and 1- and 2-methylheptafluorocyclohexa-1,3-dienes show CF=CMe stretch at 1690 and 1684 cm^{-1}, respectively [7]. The chemical shift assignments of structure (7) are then suggested.



(8) R = $CF(CF_3)_2$

The two adducts (6) and (7) are interconnected *via* cyclo-octatetraenes (9) or (10). Initial [2 + 2] addition



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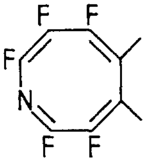
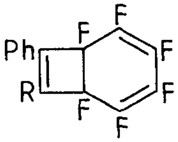


(10)

to give (6) could then result in thermal or photochemical ring opening, and reclosure to give (7). Hexafluorobenzene has been reported to undergo photochemical [2 + 2] addition of the phenylacetylenes PhC≡CR [R = H, CH_3, $CH_2CH_2CH_3$, or $C(CH_3)_3$] [9] and of propyne and but-2-yne [10] to give hexafluorobicyclo[4.2.0]octatrienes, *e.g.*, (11), initially,



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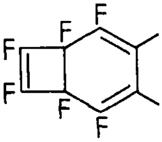

(12)

but cyclo-octatetraenes are also formed either photochemically, or in a subsequent thermal reaction. A product (12), analogous to (7), may have been formed in the but-2-yne reaction [10].

EXPERIMENTAL

Techniques were similar to those used previously [2].

Photochemical Addition of Pentafluoropyridine to But-2-yne.

Pentafluoropyridine (3.70 g, 21.9 mmol) and but-2-yne (6.91 g, 128.0 mmol) were sealed *in vacuo* in a silica ampoule

(40 cm^3) and the liquid phase was irradiated at 25 °C with u.v. light from a Hanovia UVS 500 medium-pressure mercury lamp at a distance of 25 cm for 23 days. Volatile material was then removed _in vacuo_ at -10 °C and shown by g.l.c. [2 m, 20% poly-(ethylene glycol adipate) on Celite; 20 °C for 5 min, then to 70 °C at 6 °C per min] and i.r. spectroscopy to comprise recovered but-2-yne (6.43 g, 119.1 mmol, 93%) and pentafluoropyridine (2.88 g, 17.0 mmol, 78%). The remainder was dissolved in dry carbon tetrachloride and separated by g.l.c. (4 m, 15% silicone elastomer 30 on Celite at 125 °C) to give 1,2,4,5,6-pentafluoro-7,8-dimethyl-3-azabicyclo[4.2.0]octa-2,4,7-triene (6) (nc) (0.34 g, 1.5 mmol, 7% based upon pentafluoropyridine taken) (Found: $\underline{M}^+$, 223.0431. $C_9H_6F_5N$ requires $\underline{M}$, 223.0420), 1,2,5,6,8-pentafluoro-3,4-dimethyl-7-azabicyclo[4.2.0]octa-2,4,7-triene (7) (nc) (0.08 g, 0.4 mmol, 2%) (Found: $\underline{M}^+$, 223.0428), and 1,2,5,6,8-pentafluoro-3,4,9,10-tetramethyl-7-azatricyclo[$4.2.2.0^{2,5}$]deca-3,7,9-triene (3) (nc) (0.51 g, 1.8 mmol, 8%) (Found: C, 56.1; H, 4.5; F, 34.3; N, 5.1%; $\underline{M}^+$, 277. $C_{13}H_{12}F_5N$ requires C, 56.1; H, 4.3; F, 34.5; N, 5.0%; M, 277), as a white solid, m.p. 90-92 °C (sealed tube). A brown residue (_ca._ 0.1 g) remained in the ampoule.

Hydrolysis of the 1:2 Adduct (3)

The above 7-azatricyclo[$4.2.2.0^{2,5}$]deca-3,7,9-triene (3) (68 mg, 0.25 mmol) was shaken with water (2 cm^3) at room temperature for 4 days, the mixture was extracted with chloroform (2 x 2 cm^3), and the extract was dried ($MgSO_4$) and the solvent removed to give 1,2,5,6-tetrafluoro-3,4,9,10-tetramethyl-8-oxo-7-azatricyclo[$4.2.2.0^{2,5}$]deca-3,9-diene (5) (nc) (63 mg, 0.23 mmol, 92%) (Found: F, 27.3%; $\underline{M}^+$, 275.0924. $C_{13}H_{13}F_4ON$ requires F, 27.6%; $\underline{M}$, 275.0932).

The lactam was similarly obtained from a hydrolysis with 2N-sodium hydroxide solution during 4 h.

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