Heterocyclic Polyfluoro-compounds. Part 37.[1a] Diels–Alder Reactions of Trichloro- and Trifluoro-1,2,4-triazine [1b]

By **Michael G. Barlow,*** **Robert N. Haszeldine,*** and **David J. Simpkin,** Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Trichloro-1,2,4-triazine undergoes reaction at 70 °C with the olefins: ethylene, (Z)-but-2-ene, cyclopentene, and (Z)-cyclo-octene to give the 3,4-substituted 2,6-dichloropyridine derivatives, $3,4-R_2C_5HCl_2N$, where $R_2 = H_2$ (1%), Me_2 (75%), $(CH_2)_3$ (77%), and $(CH_2)_6$ (80%), respectively, in a reaction which appears to involve initial Diels–Alder addition, and loss of nitrogen, to form an intermediate dihydropyridine. This dihydropyridine then undergoes a [1,5] sigmatropic hydrogen shift and loss of hydrogen chloride to give the pyridine, but adds a second molecule of cyclopentene to the extent of 3% in a further Diels–Alder reaction, and this is the sole pathway with bicyclo[2.2.1]hept-2-ene.

With trifluoro-1,2,4-triazine and the olefins cyclopentene, (Z)-cyclo-octene, and bicyclo[2.2.1]hept-2-ene, only products derived by addition of a second molecule of olefin to an intermediate dihydropyridine are obtained in 55, 13, and 52% yield respectively. Bis(trimethylstannyl)acetylene gives 3,4-bis(trimethylstannyl)-2,5,6-trifluoro-pyridine (11%), and bicyclo[2.2.1]hepta-2,5-diene gives 2,3,6-trifluoropyridine (43%).

THERE have been only a limited number of studies of 1,2,4-triazines as dienes in the Diels–Alder reaction. The reaction is subject to inverse electron demand, and usually requires electron-rich dienophiles,[2-4] although some success has been achieved in addition to strained double bonds.[3,5] Usually, pyridine derivatives result from addition to the 3,6-carbon atoms of the triazine ring, and loss of nitrogen, e.g. Scheme 1,[6] but pyrimidines may
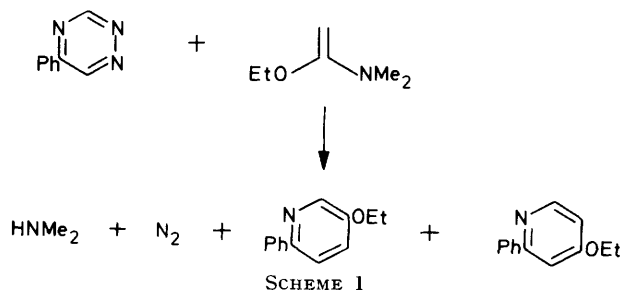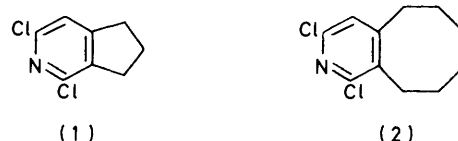
SCHEME 1

result from addition to the 1,4-ring atoms, particularly from reactions with ynamines, e.g. Scheme 2.[7,8]

The availability of trifluoro-1,2,4-triazine [9] from the flow fluorination of trichloro-1,2,4-triazine [10] over potassium fluoride prompted a comparative study of their reactions. These electron-deficient systems were found to react with simple hydrocarbon olefins.

SCHEME 2
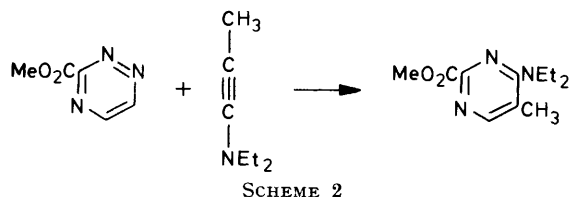
Trichloro-1,2,4-triazine reacted reluctantly with ethylene, giving 2,6-dichloropyridine in only 1% yield after 2 days at 70 °C, but reaction occurred much more readily with (Z)-but-2-ene and 2,6-dichloro-3,4-dimethylpyridine was obtained in 75% yield after 6 days at 70 °C. Similar reactivity was shown by cycloalkenes,

and cyclopentene gave the pyridine (1) (77%) and Z-cyclo-octene the pyridine (2) (80%) at 70 °C. These 2,6-dichloropyridines were unexpected, and their formation can be accounted for in terms of a [4 + 2] addition

(1)   (2)

to the triazine followed by retro-Diels–Alder loss of nitrogen (see Scheme 3 where the cyclopentene reaction is illustrated) to give a dihydropyridine (3), which undergoes the allowed [1,5] sigmatropic shift of hydrogen, when elimination of hydrogen chloride produces the dichloropyridine. This pathway is diverted to a limited extent by the [4 + 2] addition of a second molecule of cyclopentene to give the tetracyclic compound (4)
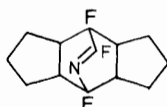
SCHEME 3
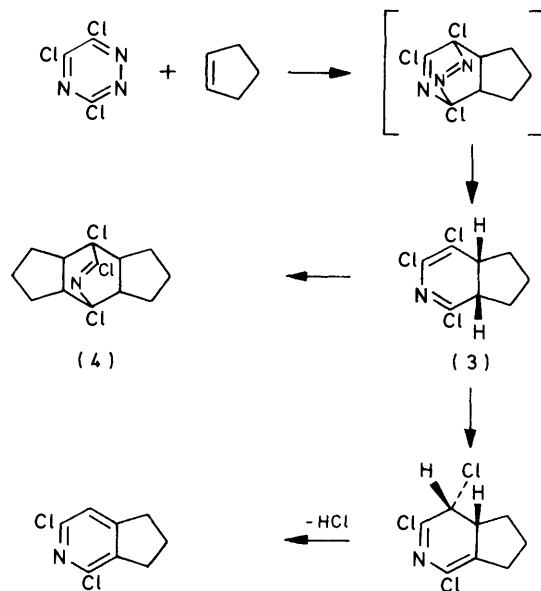
(3%). With bicyclo[2.2.1]hept-2-ene, the [1,5] sigma-tropic shift of hydrogen does not occur, presumably because this would produce a more strained double-bond, *exo* to the bicyclic system, and addition of a second molecule of olefin to give (5) (95%) occurs exclusively.
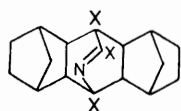

(5) X = Cl
(8) X = F

(6)

In contrast to this, trifluoro-1,2,4-triazine gave no products derived from [1,5] sigmatropic shift of hydro-gen; instead, products derived by addition of a second molecule of olefin to an intermediate 3,4-dihydropyridine were obtained exclusively, cyclopentene giving (6) (55%), (Z)-cyclo-octene giving (7) (13%), and bicyclo-[2.2.1]hept-2-ene giving (8) (52%). With bicyclo-[2.2.1]hepta-2,5-diene, the reaction involved loss of
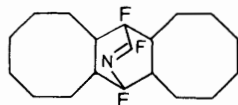

(7)
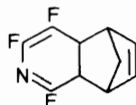
(9)

cyclopentadiene from the intermediate (9), and 2,3,6-trifluoropyridine (10) (43%) was obtained. Also, there was mass spectrometric and n.m.r. spectroscopic evidence for the limited addition of the bicycloheptadiene or of cyclopentadiene to the dihydropyridine (9). The form-ation of compound (10) formally involves the addition of the elements of acetylene to trifluoro-1,2,4-triazine, and similar reactions have been reported with other triazines.[3,5] The activated acetylene, bis(trimethyl-
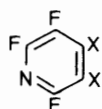

(10) X = H
(11) X = SnMe$_3$

stannyl)acetylene gave the pyridine (11) with trifluoro-1,2,4-triazine in only moderate yield (11%).

The structure of the 2,6-dichloropyridine derivatives follows readily from their spectroscopic properties. The products (6)—(8) derived from trifluoro-1,2,4-triazine clearly possessed a CF=N grouping, with $\nu_{max.}$ 1 692—1 693 cm^{-1} and δ_F 26.8—31.7 p.p.m., the low-field chemical shift being particularly characteristic of an imidoyl fluorine.[11] In the products (5) and (8) derived from bicyclo[2.2.1]hept-2-ene, the ^{13}C n.m.r. chemical shifts showed that they possessed only one type of bicyclo[2.2.1]heptane fragment and that the CX groups were attached *exo*, since the chemical shifts of the CH$_2$-

CH$_2$ carbons, 31.0 and 31.2 in (5) and 30.1 and 30.3 p.p.m. in (8), were very similar to those of bicyclo[2.2.1]-heptane itself (30.1 p.p.m.), whereas *endo*-substituents should result in an upfield shift.[12] Structure (12) is then favoured, since the alternative (13) would be impossibly crowded around the methylene bridges. These methy-lene bridge carbons, at 34.4 in (5) and 34.3 p.p.m. in (8), show an upfield shift compared to bicyclo[2.2.1]-heptane of 4.3 p.p.m., consistent with them being under
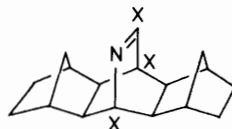
(12)
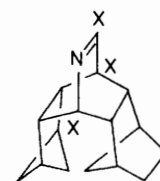
(13)

the shielding influence of the C=N bond. Compound (8) was surprisingly resistant to hydrolysis of its imidoyl fluorine,[13] being recovered unchanged after refluxing for 6 h with aqueous sodium hydroxide in tetrahydro-furan; this may reflect steric shielding of the C=N bond in (12; X = F).

In these cycloaddition reactions, the reactions with cyclopentene and cyclo-octene are noteworthy, since Diels–Alder additions to simple hydrocarbon olefins un-activated by ring-strain, are rare.[14] The combination of cycloaddition, [1,5] sigmatropic shift of hydrogen, and aromatisation by HCl elimination, seen in the trichloro-1,2,4-triazine reactions is novel, and offers scope for further study, both with this, and with other chlorine-substituted heterocycles.

In the case of trifluoro-1,2,4-triazine with olefins, the intermediate dihydropyridine undergoes cyclo-addition only. There appear to be only two examples of analogous additions to trifluoro-2-azadienes. Photo-chemical [2 + 2] addition of olefins to pentafluoro-pyridine gives an azadiene intermediate which may undergo further [4 + 2] addition,[15] and Claisen re-arrangement of tetrafluoro-4- and 3-pyridyl prop-2-enyl ethers gives intermediates which undergo intramolecular Diels–Alder addition.[16] Other examples of Diels–Alder reactions of 2-azadienes are known,[17] but additions to 1-azadienes are rare.[18]

GCD instruments). Molecular weights were obtained by mass spectrometry.

Trifluoro-1,2,4-triazine was obtained by fluorinating trichloro-1,2,4-triazine over potassium fluoride in a flow system at 450 °C.[9]

Diels–Alder Reactions of Trichloro-1,2,4-triazine.—(a) *With ethylene.* The triazine (2.0 g, 10.8 mmol) and ethylene (0.98 g, 35 mmol), sealed in a Pyrex ampoule (30 cm³) and heated at 70 °C for 2 days, gave a thick black tar. Nitrogen (5.3 mmol, 49%) and a mixture of ethylene and hydrogen chloride were removed *in vacuo*, and the residue was extracted with diethyl ether to give after removal of the solvent, trituration with light petroleum (b.p. 30—40 °C), and sublimation, 2,6-dichloropyridine [19] (15 mg, 0.09 mmol, 1%), which was identified by n.m.r.[20] and i.r. spectroscopy,[21] and contained traces of unchanged trichlorotriazine.

(b) *With (Z)-but-2-ene.* The triazine (2.0 g, 10.8 mmol) and (Z)-but-2-ene (2.27 g, 42 mmol), sealed *in vacuo* and heated at 70 °C for 6 days, gave nitrogen (1.2 mmol, 11%) and a mixture of unchanged (Z)-but-2-ene and hydrogen chloride which were removed *in vacuo*, and a brown residue. This was extracted with diethyl ether to give after removal of the solvent and sublimation at 40 °C *in vacuo*, a mixture (by g.l.c.) containing unchanged trichlorotriazine, which was hydrolysed by refluxing with water in tetrahydrofuran for 30 min. The resulting mixture was neutralised with aqueous sodium carbonate and extracted with diethyl ether; solvent was removed under reduced pressure from the extract and the residue sublimed *in vacuo* at room temperature to give 2,6-dichloro-3,4-dimethylpyridine (1.42 g, 8.1 mmol, 75%) (Found: C, 47.6; H, 3.7; Cl, 40.2; N, 8.0%; M, 175. Calc. for $C_7H_7Cl_2N$: C, 47.8; H, 4.0; Cl, 40.3; N, 8.0%; M, 175), as a white solid, m.p. 65—67 °C (lit.,[22] 61—67 °C) with δ_H (CDCl₃ solution) 7.00 (5-H) and 7.70 and 7.72 p.p.m. (3- and 4-CH₃).

(c) *With cyclopentene.* The triazine (2.0 g, 10.8 mmol) and cyclopentene (4.58 g, 67.0 mmol), sealed *in vacuo* in a Pyrex ampoule (30 cm³) and heated at 70 °C for 1.5 days gave, after removal of nitrogen (8.5 mmol, 79%), unchanged cyclopentene, and hydrogen chloride, a residue, which was extracted with diethyl ether. Solvent was removed under reduced pressure from the extract and the brown residue was sublimed to give two fractions, subliming at 50—70 °C and 70—100 °C *in vacuo*. The first fraction was resublimed to give 1,3-dichloro-6,7-dihydro-5H-2-pyridine (1) (1.56 g, 8.3 mmol, 77%) (Found: C, 51.0; H, 3.7; Cl, 37.3; N, 7.8%; M, 187. Calc. for $C_8H_7Cl_2N$: C, 51.1; H, 3.8; Cl, 37.7; N, 7.5%; M, 187), as a white powder, m.p. 33—35 °C (lit.,[23] 36 °C), δ_H (CDCl₃ solution) 7.02 (4-H), 2.93 and 2.85 (triplets, 5- and 7-CH₂), and 2.10 p.p.m. (6-CH₂); δ_C 159.6 (C-4a), 147.5 (C-1), 145.7 (C-3), 137.9 (C-7a), 119.1 (C-4), 33.1 (C-5), 30.4 (C-7), and 23.7 p.p.m. (C-6). The sp²-carbons were assigned using additive substituent parameters for substituted pyridines.[24] The second fraction was resublimed at 75 °C to give 1,7,14-*trichloro*-13-*azatetracyclo*[5.5.2.0²,⁶.0⁸,¹²]*tetradec*-13-*ene* (4) (0.1 g, 0.3 mmol, 3%) (Found: C, 53.3; H, 5.3; Cl, 36.2; N, 5.0%; M, 291. $C_{13}H_{16}Cl_3N$ requires C, 53.4; H, 5.5; Cl, 36.3; N, 4.8%; M, 291), as a white powder, m.p. 115—118 °C, $\nu_{max.}$ 1 594 cm⁻¹ (C=N str.).

(d) *With Z-cyclo-octene.* The triazine (2.0 g, 10.8 mmol) and (Z)-cyclo-octene (5.7 g, 52 mmol), sealed *in vacuo* in a Pyrex ampoule (30 cm³) and heated at 70 °C for 6 days gave, after removal of nitrogen (8.2 mmol, 76%), hydrogen

chloride, and unchanged cyclo-octene *in vacuo*, a pale brown residue which was extracted with diethyl ether. The solvent was then removed under reduced pressure, and the residue was recrystallised from light petroleum (b.p. 60—80 °C) to give 1,3-*dichloro*-5,6,7,8,9,10-*hexahydrocyclo-octa*[c]*pyridine* (2) (1.95 g, 8.64 mmol, 80%) (Found: C, 59.1; H, 5.4; Cl, 30.4; N, 6.1%; M, 229. $C_{11}H_{13}Cl_2N$ requires C, 57.4; H, 5.7; Cl, 30.8; N, 6.1%; M, 229), as colourless crystals, m.p. 42—44 °C, δ_H (CDCl₃ solution) 6.94 (4-H), 2.81 and 2.68 (triplets, 5-H and 10-H), 1.65 (6,9-H), and 1.30 p.p.m. (7,8-H); δ_C 156.7 (C-4a), 150.7 (C-1), 147.2 (C-3), 138.8 (C-10a), 123.3 (C-4), 32.9 and 31.5 (C-5,10), 28.3 and 27.2 (C-6,9), and 26.8 and 25.6 p.p.m. (C-7,8).

(e) *With bicyclo[2.2.1]hept-2-ene.* The triazine (2.0 g, 10.8 mmol) and bicyclo[2.2.1]hept-2-ene (5.5 g, 59 mmol), sealed *in vacuo* in a Pyrex ampoule (30 cm³) and heated at 70 °C for 1.5 days, deposited long needle-like crystals, and gave, after removal of nitrogen (5.9 mmol, 55%) and unchanged bicycloheptene (3.5 g, 37.2 mmol, 63% recovery) a residue which was extracted with carbon tetrachloride; solvent was removed under reduced pressure from the extract, and the resultant solid recrystallised from light petroleum (b.p. 60—80 °C) to give 1,8,16-*trichloro*-15-*azahexacyclo*[6.6.2.1³,⁶.1¹⁰,¹³.0²,⁷.0⁹,¹⁴]*octadec*-15-*ene* (5) (3.56 g, 10.3 mmol, 95%) (Found: C, 59.1; H, 5.9; Cl, 30.5; N, 4.1%; M, 343. $C_{17}H_{20}Cl_3N$ requires C, 59.2; H, 5.9; Cl, 30.9; N, 4.1%; M, 343), as colourless crystals, m.p. 200—202 °C, $\nu_{max.}$ 1 600 cm⁻¹ (C=N str.); δ_H (CDCl₃ solution) 2.67 (H-2,14), 2.47 (7,9-H), 2.12 (3,6,10,13-H), and 1.8—0.7 p.p.m. (4,5,11,12,17,18-H); δ_C 160.0 (C-16), 91.0 (C-1), 73.1 (C-8), 58.8 (C-2,7,9,14), 39.0 (C-6,10), 34.4 (C-17,18), and 31.2 and 31.0 p.p.m. (C-4,12 and C-5,11).

Diels–Alder Reactions of Trifluoro-1,2,4-triazine.—No products were obtained from attempted reactions of trifluoro-1,2,4-triazine with the following olefins (i) ethylene at 60 °C for 11 days (98% recovery); (ii) ethyl vinyl ether at room temperature for 1 week (11% recovery, with much tar formation); (iii) vinyl acetate at 70 °C for 4 days; (iv) but-2-yne at 60 °C for 1 week (88% recovery); and (v) cyclohexene at 60 °C for 1 week (95% recovery).

(a) *With bis(trimethylstannyl)acetylene.* The triazine (0.79 g, 5.85 mmol) and bis(trimethylstannyl)acetylene (2.42 g, 6.56 mmol) in tetrahydrofuran (1 cm³), sealed in a Pyrex ampoule (30 cm³) and heated at 60 °C for 18 h, gave, after removal of nitrogen (2.9 mmol, 50%) and tetrahydrofuran *in vacuo*, a brown residue, which was extracted with chloroform to give, after removal of the solvent under reduced pressure and sublimation at 60 °C *in vacuo*, 3,4-*bis(trimethylstannyl)*-2,5,6-*trifluoropyridine* (11) (0.30 g, 0.64 mmol, 11%) [Found: C, 29.3; H, 4.2; F, 11.9; N, 3.1; Sn, 51.3%; M, 461. $C_{11}H_{18}F_3NSn_2$ requires C, 28.8; H, 4.0; F, 12.4; N, 2.1; Sn, 51.7%; M, 461 (for the ¹²⁰Sn isotope)], as a white powder, m.p. 71—74 °C, with δ_H (CCl₄ solution, external benzene reference) −6.02 and 6.08 p.p.m. (2 SnMe₃, $^5J_{HF}$ 1 Hz, $^2J_{119SnH}$ 56.5 and $^2J_{117SnH}$ 54.4 Hz for both absorptions) and δ_F 21.8 (F-2, $^5J_{FF}$ 30, $^4J_{FF}$ 11 Hz), −11.4 (F-6, $^3J_{FF}$ 27 Hz), and −47.4 p.p.m. (5-F).

(b) *With cyclopentene.* The triazine (1.60 g, 11.9 mmol) and cyclopentene (4.1 g, 60.3 mmol), sealed in a Pyrex ampoule and heated at 60 °C for 6 days, gave nitrogen (5.9 mmol, 50%) and unchanged cyclopentene (2.46 g, 36.2 mmol, 60% recovery), which were removed *in vacuo*, and a dark brown oily residue; this was extracted with carbon tetrachloride. Solvent was removed under reduced pres-

sure from the extract and the residue was sublimed at 40—50 °C *in vacuo* to give 1,7,14-*trifluoro*-13-*azatetracyclo*-[5.5.2.0²,⁶.0⁸,¹²]*tetradec*-13-*ene* (6) (1.59 g, 6.55 mmol, 55%) (Found: C, 64.4; H, 6.5; F, 23.2; N, 6.0%; *M*, 243. $C_{13}H_{16}F_3N$ requires C, 64.2; H, 6.6; F, 23.5; N, 5.8%; *M*, 243) as a white powder, m.p. 61.5—63 °C, $\nu_{max.}$ 1 692 cm⁻¹ (C=N str); δ_H (CDCl₃ solution) 2.52 (2,6,8,12-H) and 1.65 p.p.m. (3,4,5,9,10,11-H); δ_F 31.7 (14-F, $^3J_{FF}$ 22 Hz), —62.5 (1-F, $^5J_{FF}$ 10 Hz), and —112.0 p.p.m. (7-F); δ_C 159.0 (C-14, $^1J_{CF}$ 306, $^2J_{CF}$ 21, $^3J_{CF}$ 17 Hz), 104.0 (C-1, $^1J_{CF}$ 208, $^3J_{CF}$ 19, $^4J_{CF}$ 4 Hz), 97.5 (C-7, $^1J_{CF}$ 214, $^2J_{CF}$ 22, $^4J_{CF}$ 4 Hz), 50.2 (C-2,12, $^2J_{CF}$ 23.5, $^3J_{CF}$ 5.9 Hz), 47.3 (C-6,8, $^2J_{CF}$ 18.9, $^3J_{CF-1}$ 8.1 Hz), 29.1 (C-3,11), 27.8 (C-5,9), and 26.4 p.p.m. (C-4,10). The tetracyclotetradecene was recovered (69%) after refluxing for 2 h with sodium hydroxide in aqueous tetrahydrofuran.

(*c*) *With* (Z)-*cyclo-octene*. The triazine (1.32 g, 9.78 mmol) and (Z)-cyclo-octene (5.65 g, 54.4 mmol), sealed in a Pyrex ampoule (30 cm³) and heated at 70 °C for 1 week, gave nitrogen (5.9 mmol, 60%) and unchanged cyclo-octene (5.31 g, 51.1 mmol, 94% recovery), which were removed *in vacuo*, and a residue which was extracted with carbon tetrachloride; solvent was removed under reduced pressure from the extract, and the resulting solid recrystallized from light petroleum (b.p. 60—80 °C) and sublimed *in vacuo* at 125 °C to give 1,10,20-*trifluoro*-19-*azatetracyclo*-[8.8.2.0²,⁹.0¹¹,¹⁸]*eicos*-19-*ene* (7) (0.42 g, 1.27 mmol, 13%) (Found: C, 69.5; H, 8.5; F, 17.4; N, 4.3%; *M*, 327. $C_{19}H_{28}F_3N$ requires C, 69.7; H, 4.3; F, 17.4; N, 4.3%; *M*, 327), a white powder, m.p. 140—143 °C, $\nu_{max.}$ 1 693 (C=N str.); δ_F (CDCl₃ solution) 27.4 (F-20, $^3J_{FF}$ 23 Hz), —55.2 (F-1), and —103.8 (F-10).

(*d*) *With bicyclo*[2.2.1]*hept-2-ene*. The triazine (1.40 g, 10.4 mmol) and bicyclo[2.2.1]hept-2-ene (7.00 g, 74.5 mmol), sealed in a Pyrex ampoule (30 cm³) and heated at 70 °C for 1 week, gave nitrogen (5.2 mmol, 50%) and un-changed bicycloheptene (4.97 g, 52.9 mmol, 71% recovery) which were removed *in vacuo*, and a pale brown residue; this was extracted with carbon tetrachloride. Solvent was removed under reduced pressure from the extract, and the residue sublimed at 100 °C *in vacuo* and recrystallized from methanol to give 1,8,16-*trifluoro*-15-*azahexacyclo*-[6.6.2.1³,⁶.1¹⁰,¹³.0²,⁷.0⁹,¹⁴]*octadec*-15-ene (8) (1.60 g, 5.41 mmol, 52%) (Found: C, 69.0; H, 7.1; F, 19.3; N, 4.8%; *M*, 295. $C_{17}H_{20}F_3N$ requires C, 69.1; H, 6.8; F, 19.3; N, 4.8%; *M*, 295), as colourless crystals, m.p. 144—145 °C, $\nu_{max.}$ 1 693 cm⁻¹ (C=N str.); δ_H (CCl₄ solution) 2.48 (2,14-H), 2.38 (7,9-H), 2.02 (3,13-H), 1.98 (6,10-H), and 1.8—0.8 p.p.m. (4,5,11,12,17,18-H); δ_F 26.8 (F-16, $^3J_{FF}$ 22 Hz), —60.0 (F-1), and —112.5 p.p.m. (8-F, $^5J_{FF}$ 9 Hz); δ_C (CDCl₃ soln., insufficient scans were recorded to show absorptions for C-1, -8, and -16) 52.5 (C-2,14, $^2J_{CF}$ 25.5, $^3J_{CF}$ 6.1 Hz), 52.3 (C-7,9, $^2J_{CF}$ 19.2; $^3J_{CF}$ 7.1 Hz), 37.2 (C-3,13), 36.4 (C-6,10), 34.3 (C-17,18), and 30.3 and 30.1 p.p.m. (C-4,13 and C-5,11).

The hexacyclo-octadecene was recovered (96%) un-changed after being refluxed for 6 h with sodium hydroxide in aqueous tetrahydrofuran.

(*e*) *With bicyclo*[2.2.1]*hepta-2-5-diene*. The triazine (1.06 g, 7.85 mmol) and bicyclo[2.2.1]hepta-2,5-diene (5.69 g, 61.8 mmol) were sealed in a Pyrex ampoule (30 cm³) and heated at 70 °C for 3 days. The volatile material was then removed *in vacuo* and shown by g.l.c. (2 m trixylyl phosphate on Celite at 100 °C) to comprise four components in the ratio 1 : 93 : 1 : 5, the major component being the

bicycloheptadiene. Preparative g.l.c. gave as the last eluted 2,3,6-trifluoropyridine (0.45 g, 3.37 mmol, 43%) (Found: C, 44.8; H, 1.6; F, 42.3; N, 10.7%; *M*, 133. Calc. for $C_5H_2F_3N$: C, 45.1; H, 1.5; F, 42.8; N, 10.5%; *M*, 133) as a colourless liquid, b.p. 109—115 °C (Siwoloboff, lit.[25] 115—116 °C); δ_H (neat liquid) 7.4 (4-H), and 6.5 (5-H); δ_F 3.1 (2-F), —11.2 (6-F), and —69.9 (3-F).[25] The dark brown residue was extracted with carbon tetra-chloride, and chromatographed on alumina with light petroleum (b.p. 30—40 °C) elution to give an oily solid (70 mg), which contained cyclopentadiene dimer (i.r.). Recrystallization from light petroleum (b.p. 30—40 °C) at —20 °C gave colourless crystals (50 mg), which were sublimed *in vacuo* at 60 °C, and shown by g.l.c. and ¹⁹F n.m.r. spectroscopy to comprise two major components in the ratio 2 : 3, with δ_F ca. 19.2 (N=CF), —61.1 and —61.5 (CF–N), and —111.9 and —113.5 (C–CF). G.l.c. coupled mass spectrometry indicated that the first component contained one cyclopentadiene and one bicycloheptadiene residue (Found: *M*, 265. Calc. for $C_{15}H_{18}F_3N$: *M*, 265) and the second contained two bicycloheptadiene residues (Found: *M*, 291. Calc. for $C_{17}H_{20}F_3N$: *M*, 291).

The volatile product from a similar reaction was treated with bromine, when fractionation *in vacuo* yielded 2,3,6-trifluoropyridine (35%).

REFERENCES

[1] (*a*) Part 36, M. G. Barlow, B. Coles, and R. N. Haszeldine, *J. Fluorine Chem.*, 1980, **15**, 397; (*b*) preliminary communication, M. G. Barlow, R. N. Haszeldine, and D. J. Simpkin, *J. Chem. Soc., Chem. Commun.*, 1979, 658.

[2] H. Neunhoeffer and H.-W. Frühauf, *Tetrahedron Lett.*, 1969, 3151; *ibid.*, 1970, 3355; *Liebigs Ann. Chem.*, 1972, **758**, 120; *ibid.*, p. 125.

[3] W. Dittmar, J. Sauer, and A. Steigel, *Tetrahedron Lett.*, 1969, 5171.

[4] A. Steigel and J. Sauer, *Tetrahedron Lett.*, 1970, 3357.

[5] J. A. Eli, W. S. Wilson, and R. N. Warrener, *Tetrahedron Lett.*, 1970, 1837; *Aust. J. Chem.*, 1972, **25**, 865.

[6] B. Burg, W. Dittmar, H. Reim, A. Steigel, and J. Sauer, *Tetrahedron Lett.*, 1975, 2897.

[7] H. Reim, A. Steigel, and J. Sauer, *Tetrahedron Lett.*, 1975, 2901.

[8] H. Neunhoeffer and B. Lehmann, *Liebigs Ann. Chem.*, 1977, 1413.

[9] M. G. Barlow, R. N. Haszeldine, C. Simon, D. J. Simpkin, and G. Ziervogel, following paper.

[10] C. Cristescu and J. Marcus, *Pharmazie*, 1961, **16**, 135; P. K. Chary and T. L. V. Ulbricht, *J. Am. Chem. Soc.*, 1958, **80**, 976; B. A. Loving, C. E. Synder, G. L. Whittier, and K. R. Fountain, *J. Heterocycl. Chem.*, 1971, **8**, 1095.

[11] J. W. Emsley and L. Phillips, *Proc. Nucl. Magn. Reson. Spectrosc.*, 1971, **7**, 255.

[12] F. W. Wehrli and T. Wirthlin, ' Interpretation of Carbon-13 N.M.R. Spectra,' Heyden, London, 1978, p. 38.

[13] R. E. Banks and C. Oppenheim, *J. Fluorine Chem.*, 1978, **12**, 27.

[14] J. Sauer, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 211.

[15] M. G. Barlow, D. E. Brown, and R. N. Haszeldine, *J. Chem. Soc., Chem. Commun.*, 1977, 669; *J. Chem. Soc., Perkin Trans. 1*, 1978, 363; M. G. Barlow, D. E. Brown, R. N. Haszeldine, and J. R. Langridge, *J. Chem. Soc., Perkin Trans. 1*, 1980, 129.

[16] G. M. Brooke, R. S. Matthews, and N. S. Robson, *J. Chem. Soc., Perkin Trans. 1*, 1980, 102.

[17] K. K. Chen and C. K. Bradsher, *J. Org. Chem.*, 1979, **44**, 4680; P. H. Daniels, J. L. Wong, J. L. Atwood, L. G. Canada, and R. D. Rogers, *J. Org. Chem.*, 1980, **45**, 435; J. Hamer, ' 1,4-Cycloaddition Reactions,' Academic Press, New York, 1967.

[18] Y.-S. Cheng, F. W. Fowler, and A. T. Lupo, *J. Am. Chem. Soc.*, 1981, **103**, 2090, and references cited therein.

[19] F. W. Dootson and W. J. Sell, *J. Chem. Soc.*, 1900, **77**, 238.

[20] C. J. Pouchert, ' The Aldrich Library of Infrared Spectra,' 2nd edn., 1975, spectrum 1146B.

[21] C. J. Pouchert and J. R. Campbell, ' The Aldrich Library of N.M.R. Spectra,' 1974, vol. 9, spectrum 13A.

[22] M. M. Robison, *J. Am. Chem. Soc.*, 1958, **80**, 5481.

[23] V. Prelog and O. Metzler, *Helv. Chim. Acta*, 1946, **29**, 1170.

[24] Ref. 12, p. 49.

[25] R. D. Chambers, F. G. Drakesmith, and W. K. R. Musgrave, *J. Chem. Soc.*, 1965, 5045.