

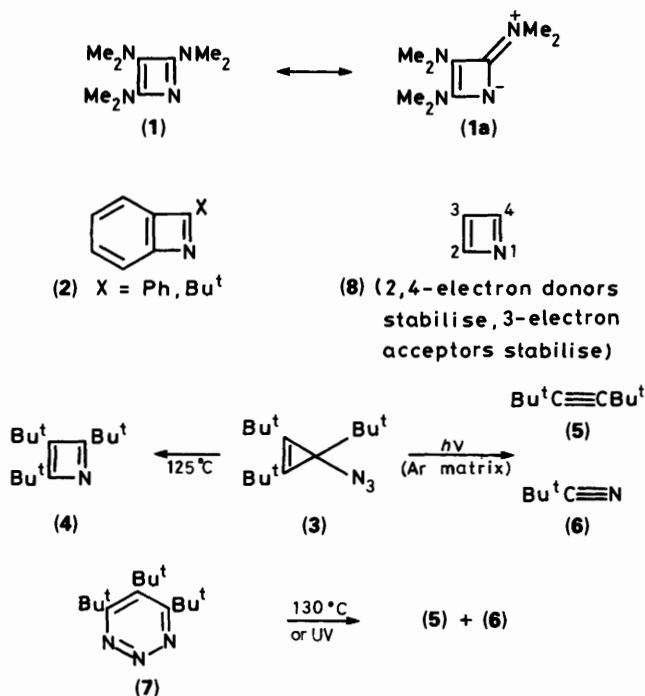
Photochemistry of Halogenocarbon Compounds. Part 5.¹⁻² Photolysis of Fluorinated 1,2,3-Triazine Derivatives

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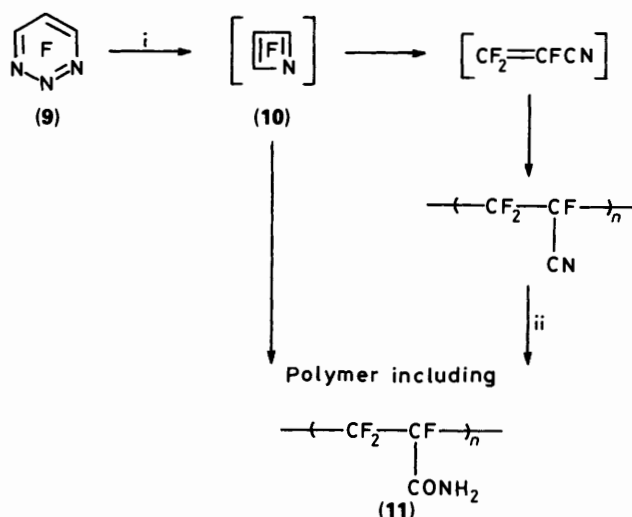
Photolysis experiments are described on perfluoro-1,2,3-triazine (9) and its corresponding perfluoro-isopropyl derivatives. A polymer was obtained from (9) but a dimer of perfluoro-2,4-di-isopropyl-azete (16) is obtained, from (15) quantitatively. The *endo* structure of the dimer is revealed by formation of a stable carbanion on addition of CsF. Trapping of the azete (16) with furan gave interconvertible 1:1 cycloaddition products. Products consistent with co-dimerisation of azetes are described.

There is, of course, considerable interest in 4π -anti-aromatic systems but azetes have received much less attention than cyclobutadiene derivatives.³ Observable azetes have been described, *i.e.* the push-pull system (1) of Gompper and co-workers,⁴ although this might be regarded by some as a dipolar species (1a); the stable benzazete system, *e.g.* (2) of Rees and Storr,⁵ and, more recently (*i.e.* after the present work began), Regitz and co-workers⁶ have described the remarkably stable tri-*t*-butyl-azete (4) obtained, surprisingly, by pyrolysis of the azide (3), whereas photolysis of (3) even in an argon matrix led to (5) and (6). Calculations⁷ on azetes have suggested that azete (8) is less anti-aromatic than cyclobutadiene and that electron-donating substituents at the 2,4-positions stabilise, while electron-accepting substituents at the 3-position would also stabilise. The position of azetetrahedrane on the energy surface has also been discussed on the basis of calculations.⁸



It is now well established that perfluoroalkyl groups have a dramatic stabilising influence on small rings^{9,10} and, in earlier parts of this series, we have been describing the stabilisation of

some remarkable valence isomers of aromatic systems, through extensive substitution by perfluoroalkyl groups. We have also been exploring the effect of fluorine and of perfluoroalkyl groups as substituents on the generation and reactivity of corresponding azetes. Earlier approaches suggested the formation of an azete in the photolysis of perfluoro-3,5-di-isopropylpyridazine,¹¹ and we subsequently explored photolysis of perfluoroalkyl-1,2,4-triazine derivatives¹² as a rational approach to the generation of azetes. Here, however, we describe the successful generation of azetes from perfluorinated derivatives of the 1,2,3-triazine system, which were described recently in work from this laboratory.¹³



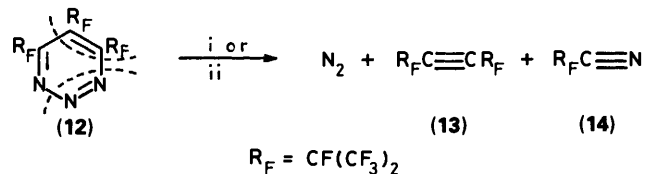
Conditions: i, $h\nu$, 254 nm; ii, atmospheric moisture.

Photolysis of trifluoro-1,2,3-triazine (9) at 254 nm gave a polymer (11), which was insoluble in common solvents; solution ($\text{CF}_2\text{ClCFCl}_2$) and vapour phase conditions gave the same result. Elemental analysis indicated loss of nitrogen and no absorptions corresponding to $\text{C}\equiv\text{N}$ were evident. Furthermore, the IR spectrum bore a close similarity to that revealed for polytrifluoroacrylonitrile, after hydrolysis, which occurred very readily indeed.¹⁴ We assume, therefore, that a similar process has occurred in our system. Attempts were made to trap trifluoroazete (10) with furan and with hexafluorobut-2-yne, but no unambiguous evidence for trapping at ambient temperatures was observed. Some incorporation of hexafluorobut-2-yne into

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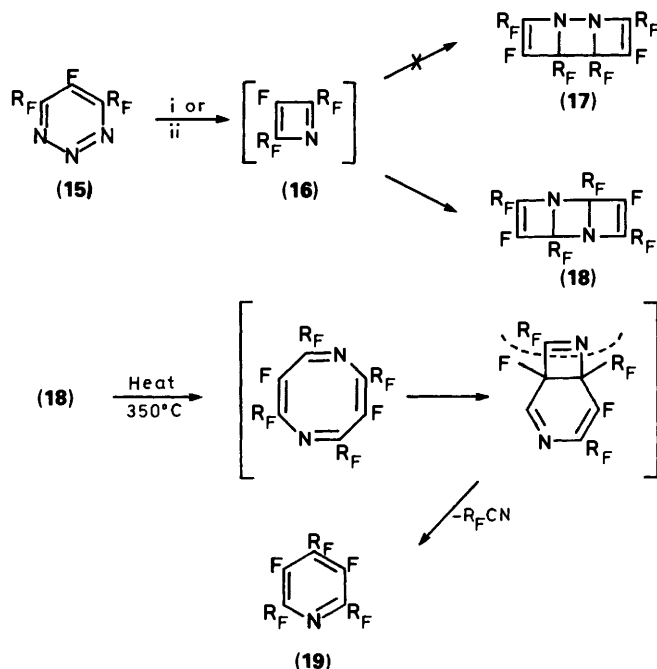
the polymer was evident and a small amount (<5%) of a volatile component was detected whose mass spectrum was consistent with a 1:1 adduct of (10) and hexafluorobut-2-yne.

Photolysis of the perfluorotri-isopropyl derivative (12) was disappointing, in that simple fragmentation to a mixture of the alkyne derivative (13) and the nitrile (14) was obtained. This is, however, quite consistent with observations with other systems [see (7)].⁶



Conditions: i, hv, 254 nm, $\text{CF}_2\text{ClCFCl}_2$; ii, hv, 254 nm, 10^{-2} mmHg.

Remarkably, photolysis of the di-isopropyl derivative (15) under a variety of conditions gave quantitative conversion into a compound, whose elemental analyses and spectroscopic data corresponded to a dimer of an intermediate azete (16). The IR and ¹⁹F NMR spectra clearly revealed that dimerisation occurred through reaction at C=N, because fluorine atoms at vinylic positions are readily distinguished from the highfield fluorine resonances that are characteristic of fluorine at tertiary sites. However, distinction between (17) and (18) was only possible on pyrolysis, where little reaction occurred until 350 °C but then smooth conversion into the known pyridine derivative (19)¹⁵ took place. This is significant because structure (17)



Scheme 1. Conditions: i, hv, 254 nm; ii, hv, 254 nm, transference conditions, 8 mmHg.

could not give the substitution pattern observed for (19). No isomerisation of (18) was observed before fragmentation, and this corresponds with observations of Paquette and co-workers,¹⁶ who reported that valence isomers of cyclo-octatetraene, substituted with t-butyl groups, fragment before isomerisation.

The interesting question arises as to whether (18) is formed as the *endo* (18a) or the *exo* (18b) isomer and in other $2\pi + 2\pi$ cycloadditions involving C=N bonds the *exo* isomer has been described.¹⁷ Various approaches to structure proof for (18)

were explored which attempted further ring closure: (a) compound (18) was inert to further irradiation, with or without sensitizers (a $2\pi + 2\pi$ cycloaddition would have given a diazabicyclic structure); (b) no cyclisation occurred with potassium fluoride at a variety of temperatures; but (c) on reaction with caesium fluoride a stable, observable anion (20) was produced which was trapped with chlorine (28), and this ring closure is only possible for the *endo* structure (18a) (Scheme 2). The ¹⁹F NMR data for the anion (20a) are unambiguous because vinylic fluorine observed in (18a), has disappeared, and been replaced by CF_2 and an additional tertiary fluorine. The latter is, however, shifted *downfield* from the characteristic position because of the adjacent charge and this is a pattern now well established with other observable fluorinated anions.¹⁸

It is worth emphasising that the dimer (18) does, in fact, constitute a rare example of an authentic 1,3-diazetidene ring,^{17,19} and this is significant because some of the examples of this system claimed in the literature have been questioned.²⁰

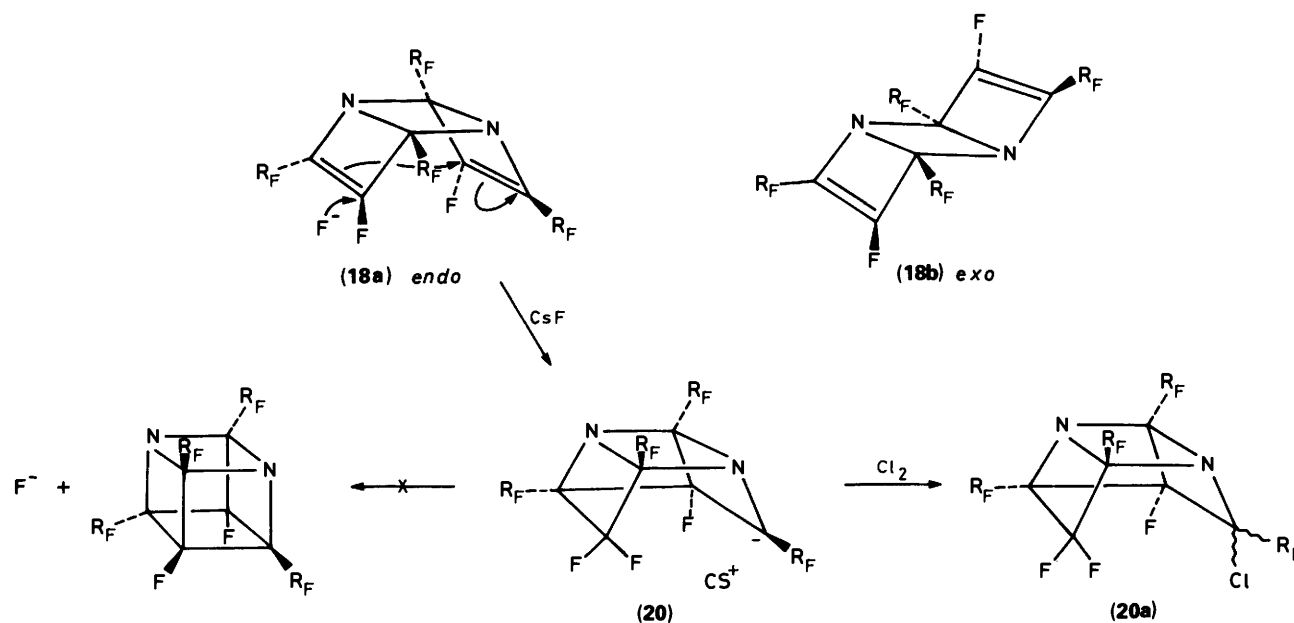
We have been able to trap the azete (16), by photolysis of (15) in the presence of furan and three isomeric compounds were identified in the product, each of which corresponded to 1:1 adducts; compound (23) was isolated pure but compounds (21) and (22) could not be separated. The structures of (21)–(23) derive principally from NMR data and addition to C=C and C=N of the azete (16) is immediately distinguishable by the presence, or otherwise, of a fluorine resonance arising from $\text{CF}=\text{C}$. This is absent from the spectra of (21) and (22) but a characteristic highfield resonance arising from a tertiary fluorine occurs in the spectrum of (22) (–174 ppm); a corresponding resonance occurs in the spectrum of (21) but this is to lower field (–150 ppm) and the different shifts probably derive from an effect of oxygen. In contrast, the fluorine spectrum of (23) reveals the presence of $\text{C}=\text{CF}$ (–97 ppm). The distinction between 2,3- and 2,5-addition to the furan entity is clearly discernible by comparisons with NMR data obtained from 2,3- and 2,5-adducts to other systems.²¹ Such comparisons therefore establish that (22) and (23) both involve 2,3-additions and compound (21) involves a 2,5-addition to the furan moiety. This then leaves the question of *exo*- or *endo*-arrangements. Most revealing is the fact that both (21) and (22) are smoothly converted into (23), by passage through a gas chromatography column at 160 °C, although static pyrolysis at the same temperature gave a complex mixture of products. Interconversion of this type is most readily understood if each of the isomers (21)–(23) has the *endo*-relationship and undergoes Cope interconversion as illustrated in Scheme 3. Additionally, comparison of chemical shifts of the tertiary fluorine in structure (21), with data from the *exo*-adduct²² obtained by the reaction of the Dewar isomer of hexafluorobenzene with furan, showed that a chemical shift of –150 ppm for (21) is only consistent with the *endo*-structure (21).

Although trapping of the azete (16) (with furan) failed, photolysis of a mixture containing trifluoro-1,2,3-triazine (9) and the perfluorodi-isopropyl derivative (15) gave a product mixture (Scheme 4) consistent with co-dimerisation of the azetes (9) and (16). In addition to the products obtained separately by generating these azetes [*i.e.* hydrolysed polymer (11) and dimer (18), respectively], trifluoro-1,3,5-triazine (25) and the known²³ pyridine derivative (27) were obtained. These are clearly consistent with the intermediacy of the adduct (24), prior to the fragmentation indicated in Scheme 4.

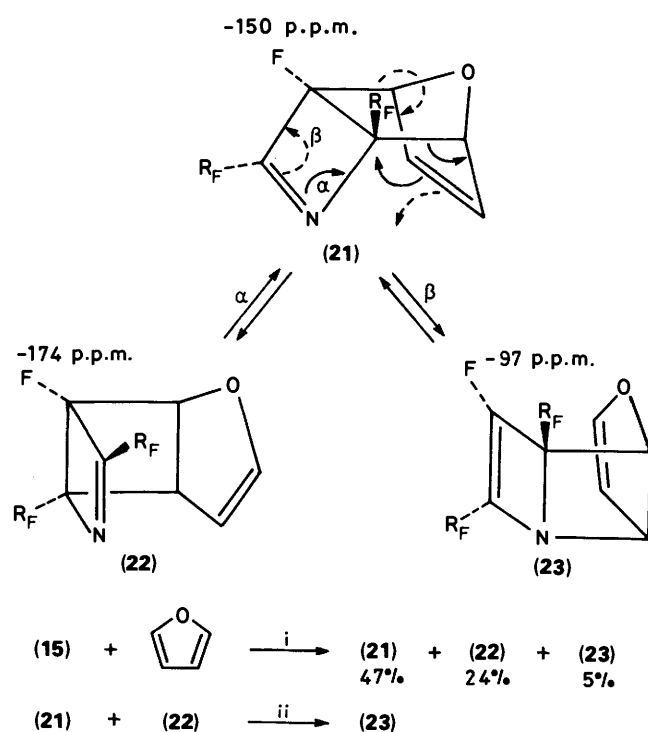
The accompanying paper²⁴ not only reveals additional evidence for the formation of the azetes (10) and (16), but also describes direct observation of the species.

Experimental

Instrumentation has been described elsewhere.¹³ Chemical shift



Scheme 2.



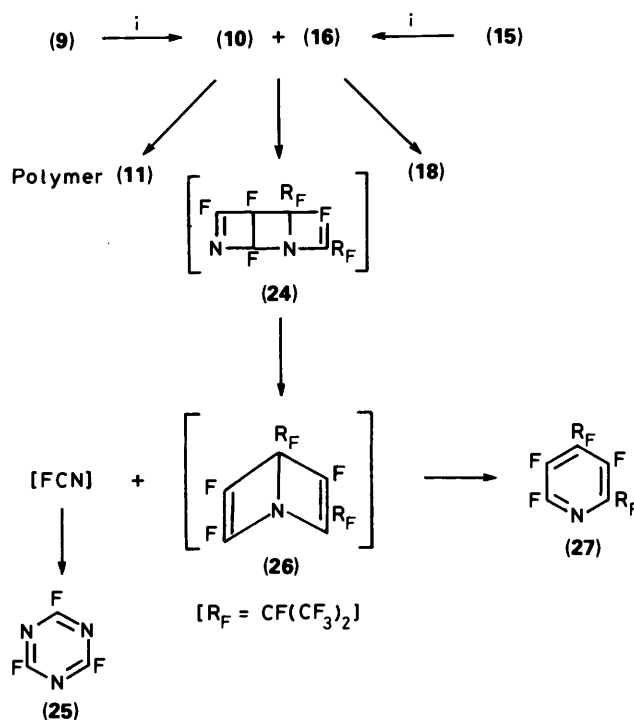
Scheme 3. Reagents and conditions: *i*, $h\nu$, 254 nm, $\text{CF}_2\text{ClCFCl}_2$; *ii*, 160 °C, GLC (polyfluorinated stationary phase).

for (^{13}C s) is quoted as positive in ppm downfield from caesium fluoride in water.

General Procedure for Photochemical Reactions

Appropriate quantities of reactant(s) and solvent (if any) were placed in a quartz tube (of variable volume), cooled to low

* As an alternative to the flame sealing of quartz tubes under vacuum, a Teflon vacuum tap (Rotoflo) may be attached to a quartz tube by means of a graded Pyrex/quartz seal. Such tubes are immediately reusable after cleaning.



Scheme 4. Conditions: *i*, $h\nu$, 254 nm.

temperature (liquid air) under high vacuum (10^{-2} Torr). The tube was sealed,* allowed to come to room temperature, and irradiated at 253.7 nm (low pressure arcs), for a given length of time. The tube was cooled (liquid air), a nitrogen atmosphere introduced, gaseous products were removed by careful transference (generally 10–200 Torr) into a cold trap. Volatile liquid products were then isolated by transference at high vacuum (10^{-2} Torr) and, where appropriate, purified by further micro-distillation or preparative gas chromatography. Polymeric materials were removed from glass surfaces manually.

(1) Trifluoro-1,2,3-triazine (9)¹³: see also Table 1 (with Peter Hoare).—(i) Vapour phase. Trifluoro-1,2,3-triazine (9) (0.25 g,

Table 1. Photochemical reactions of trifluoro-1,2,3-triazine (**9**).

Reactant(s)	Tube volume (cm ³)	Irradiation ^b time (253.7 nm)	Products
(i) (9) (0.25 g, 1.85 mmol)	20	7 d	Light brown polymer (11) (0.15 g)
(ii) (9) (1.0 g, 7 mmol) ^a	50	2 d	Light brown polymer (11) unchanged (9)
(iii) (9) (0.4 g, 3.0 mmol) hexafluorobut-2-yne (1.9 g, 11.7 mmol)	300	63 h	Light brown polymer (0.2 g) ^e
(iv) (9) (1.5 g, 11.1 mmol)	3 000	6 h	Multicomponent mixture ^f

^a Plus solvent, 1,1,2-trichloro-1,2,2-trifluoroethane (23 ml). ^b Ambient temperature *ca.* 40 °C. ^c C₃F₃N requires C, 33.6; F, 53.3; N, 13.1; C₃F₃H₂NO requires C, 28.8; F, 45.6; N, 11.2; C₂F₂N requires C, 31.6; F, 50.0; N, 18.4%. ^d Measured by Differential Scanning Calorimetry, poly(trifluoroacrylonitrile) decomposes 145 °C;¹⁴ IR for polytrifluoroacrylonitrile: ν_{\max} : broad bands centred on 3 300m (NH), 1 710s (C=O), 1 370m sh, and 1 100s cm⁻¹ (C-F).¹⁴ ^e IR spectrum ν_{\max} : broad bands centred on 3 400m, 2 800w, 1 700m, 1 350m, and 1 200s cm⁻¹; mass spectrum, *m/z* (%): 269 (75, C₇F₉N), 250 (38, C₇F₉N - F), 219 (21, C₇F₉N - CF₂), 200 (47, C₇F₉N - CF₃), and 69 (100, CF₃). ^f Includes one component (*ca.* 5% yield); mass spectrum, *m/z* (%): 269 (24, C₇F₉N), 250 (17, C₇F₉N - F), 219 (16, C₇F₉N - CF₂), 200 (31, C₇F₉N - CF₃), and 69 (100, CF₃).

1.85 mmol) in a quartz tube (20 ml) after irradiation (7 days) gave a light brown polymer (**11**) (0.15 g). This material was insoluble in the common halogenated solvents and acetonitrile, and only sparingly soluble in acetone. Spectroscopic data is shown in Table 1.

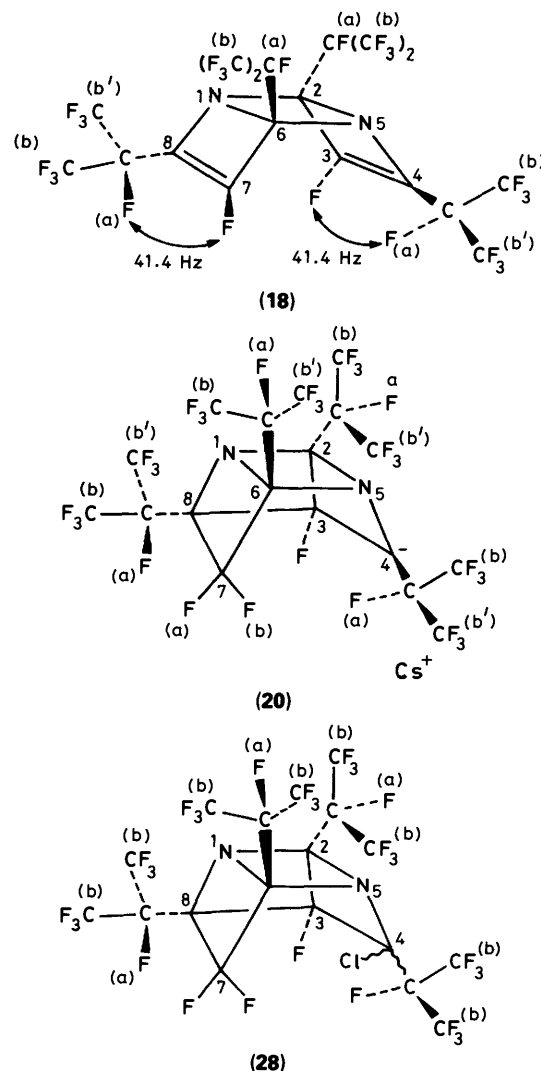
Reactions done in the liquid phase, and in the presence of hexafluorobut-2-yne are shown in Table 1.

(2) *Perfluoro-4,5,6-tri-isopropyl-1,2,3-triazine (12)*.¹³—(i) *Vapour phase*. Perfluoro-4,5,6-tri-isopropyl-1,2,3-triazine (**12**) (0.16 g, 0.27 mmol) in a quartz tube (25 cm³), after irradiation (72 h), gave a gaseous product (0.15 g), consisting of perfluoroisobutyronitrile (**14**)¹² and perfluoro-2,5-dimethylhex-3-yne (**13**)¹² in equal quantities (30% yield), and unchanged perfluoro-4,5,6-tri-isopropyl-1,2,3-triazine (**12**) (64%).

(ii) *Solution phase*. Perfluoro-4,5,6-tri-isopropyl-1,2,3-triazine (**12**) (0.2 g, 0.34 mmol) and 1,1,2-trichloro-1,2,2-trifluoroethane (2 ml) were sealed in a quartz NMR tube under high vacuum, and irradiated (4 h). The product (0.19 g) consisted of perfluoroisobutyronitrile (**14**)¹² and perfluoro-2,5-dimethylhex-3-yne (**13**)¹² in quantitative yield.

(3) *Perfluoro-4,6-di-isopropyl-1,2,3-triazine (15)*.¹³ *see also Table 2.*—(A) (i) *Liquid phase*. Perfluoro-4,6-di-isopropyl-1,2,3-triazine (1.0 g, 2.3 mmol) and 1,1,2-trichloro-1,2,2-trifluoroethane (15 g) in a quartz tube (50 cm³), were irradiated for 8 h. The solvent was evaporated under reduced pressure (20 Torr), and the residual oil purified by microdistillation (10⁻² Torr) to give perfluoro-2,4,6,8-tetraisopropyl-1,5-diazatricyclo-[4.2.0.0^{2,5}]octa-3,7-diene (**18**) (0.93 g, 99%) as a colourless viscous liquid (Found: C, 26.7; F, 69.8; N, 3.6. C₁₈F₃₀N₂ requires C, 26.5; F, 70.0; N, 3.4%); δ_F 76.05 (6 F, s, 4b-, 8b-F or 4b', 8b'-F), 76.66 (12 F, s, 2b-, 6b-F), 77.35 (6 F, s, 4b', 8b' or 4b, 8b-F), 112.0 (1 F, d, *J* 41.4 Hz, 3- or 7-F), 113.0 (1 F, d, *J* 41.4 Hz, 7- or 3-F), 185.33 (2 F, sept, *J*, 6.4 Hz, 2a, 6a-F), and 185 [2 F, d, (*J*, 41.4 Hz) of sept (*J* 6.4 Hz), 4a, 8a-F]; ν_{\max} 1 650 cm⁻¹ (C=C); *m/z* (%) 645 [*M*⁺ - CF(CF₃)₂], 550 [*M*⁺ - CF₃ - (CF₃)₂CF - CN], 500 (19), and 69 (100, CF₃).

(ii) *Under transference conditions (with Peter Hoare)*. Perfluoro-4,6-di-isopropyl-1,2,3-triazine (**15**) (1.0 g, 2.3 mmol) was placed in a large transference vessel (silica, 36 × 10 cm) to which a side arm and cold trap were attached. The transference vessel was cooled (liquid air), evacuated, and the pressure was set to 8 mmHg (nitrogen). The system was allowed to warm, the attached trap was cooled (liquid air), and the vessel and contents were irradiated for 24 h, whilst under transference;



after this time all the material had been transferred to the cold trap. The trapped material (0.82 g) was shown by GLC (capillary) to consist of mainly one component, identified as (**18**) (0.81 g, 86%).

Table 2. Photochemical reactions of perfluoro-4,6-di-isopropyl-1,2,3-triazine (15).

	Reactants (g; mmol)		CF ₂ ClCFCl ₂ (solvent) (g)	Tube volume (cm ³)	Irradiation ^c time (h)	Products (g; %)				
	(15)	furan				(18)	(21) + (22) ^a	(23)	(15)	Others
(A)										
(i)	1.0, 2.3	—	15	50	8	0.93; 99	—	—	—	—
(ii)	1.0, 2.3	—	—	ca. 2 800 ^d	24	0.81; 86	—	—	—	—
(iii)	0.3, 0.7	—	—	300	95	0.145; 52	—	—	—	(14) (0.01; 7)
(B)										
(i)	0.35; 0.8	2; 29.4	5	50	15	—	0.22; 37, 19 (47, 25) ^b	0.015; 4 (5) ^b	0.06; 19	—
(ii)	0.5, 1.1	2; 29.4	5	50	15	—	0.27; 32, 16 (54, 27) ^b	0.015; 3 (5) ^b	0.2; 40	—
(iii)	0.2, 0.46	1.14; 16.8	2.8	50	15	—	0.13; 40, 20 (50, 25) ^b	0.01; 4.5 (6) ^b	0.04; 20	—
(iv)	0.35, 0.8	2; 29.4	8.5	100	15	—	0.27; 48, 23 (53, 26) ^b	0.015; 4 (4.5) ^b	0.035; 10	—
(v)	0.35, 0.8	2; 29.4	5	50	8	—	0.17; 28, 14 (45, 22) ^b	0.012; 3 (5) ^b	0.12; 35	—

^a Inseparable mixture. ^b (Yields) calculated from amount (15) consumed. ^c 253.7 nm. ^d Transference conditions.

(B) *In the presence of furan.* (i) Perfluoro-4,6-di-isopropyl-1,2,3-triazine (15) (0.35 g, 0.8 mmol), 1,1,2-trichloro-1,2,2-trifluoroethane (5 g), and furan (2.0 g, 29.4 mmol), in a quartz tube (50 cm³) were irradiated (253.7 nm) for 15 h. After introduction of a nitrogen atmosphere, the solution was filtered to remove polymeric material and excess of furan and solvent were removed. The residual oil was further purified by transference into a cold trap (10⁻² Torr) to give the product (0.31 g) as a yellow oil. Analysis of the oil (capillary GLC) revealed the presence of unchanged triazine (15) (0.06 g), removed by careful vacuum transference (50 Torr), and two major components. These last two products were separated by microdistillation (10⁻² Torr), and found to consist of: (i) (more volatile component) an inseparable mixture of endo-1-fluoro-2,4-diheptafluoroisopropyl-9-oxa-3-azatricyclo[4.2.1^{5,8,0}]octa-2,6-diene (21) and endo-1-fluoro-7,9-diheptafluoroisopropyl-3-oxa-8-azatricyclo[5.2.0.0^{2,6}]nona-4,8-diene (22) as a colourless liquid (0.22 g, 47% (21) and 24% (22) respectively; δ_F (CDCl₃) (21) 73.35 (3 F, m, J, 9 Hz, 4b- or 4b'-F), 73.82 (6 F, d, J 6 Hz, 2b-F), 75.60 (3 F, m, J 9 Hz, 4b'- or 4b-F), 150 (1 F, s, 1-F), -186.16 (1 F, m, J 6 Hz, 2a-F), 186.69 (1 F, m, J 9 Hz, 4a-F); δ_F (CDCl₃) (22) 71.74 (3 F, m, 9b-F), 72.45 (3 F, m, J 10 Hz, 7b-F), 74.81 (3 F, m, 9b'-F), 75.60 (3 F, m, 7b'-F), 174.44 (1 F, bs, 1-F), 179.16 (1 F, m, 9a-F), 189.89 (1 F, m, J 10 Hz, 7a-F). δ_H (CDCl₃) (21) 6.41 (1 H, s, 6- or 7-H), 63.7 (1 H, s, 7- or 6-H), 5.38 (1 H, d, J 10 Hz, 5-H), and 4.99 (1 H, d, J, 2.5 Hz, 8-H); δ_H (CDCl₃) (22) 5.17 (1 H, s, 4-H), 5.04 (1 H, s, 5-H), 4.04 (1 H, d, J 10.6 Hz, 2- or 6-H), and 4.02 (1 H, d, J 10.6 Hz, 6- or 2-H); mixture of (21) and (22) *m/z* (%) 475 (12, M⁺), 447 (18, M⁺ - CO), 446 (100, M⁺ - CHO), 406 (12, M⁺ - CF₃), 378 (20, M⁺ - CO - CF₃), 337 (12, M⁺ - CHO - CF₃), 306 [24, M⁺ - CF(CF₃)₂], 69 (88, CF₃), and 68 (63, C₄H₄O); ν_{max} [liquid film, mixture of (21) and (22)] 1 670 [w, HC=CH (21)], 1 635 [w, HC=CH (22)], and 1 600 cm⁻¹ [m, C=N/CH=CH (22)].

(ii) (Less volatile component) endo-9-fluoro-1,8-diheptafluoroisopropyl-3-oxa-7-azatricyclo[5.2.0.0^{2,6}]nona-4,8-diene (23) as a colourless liquid (0.015 g, 5%); δ_F (CDCl₃) 77.97 (3 F, m, 1b- or 1b'-F), 78.28 (3F, m, 1b'- or 1b-F), 79.28 (3 F, m, 8b'- or 8b-F), 80.29 (3 F, m, 8b'- or 8b-F), 97.30 (1 F, d, J, 76 Hz, 9-F), 186.08 (1 F, d, J, 76 Hz, 8a-F), and 187.14 (1 F, m, 11a-F); δ_H (CDCl₃) 5.89 (1 H, d, J 5.8 Hz, 4- or 5-H), 5.82 (1 H, d, J 5.8 Hz, 5- or 4-H), 5.63 (1 H, br s, 2- or 6-H), and 5.38 (1 H, d, J 6.7 Hz, 6- or 2-H); *m/z* (%) 475 (7, M⁺), 456 (7, M⁺ - F), 447 (14, M⁺ - CO), 446 (100, M⁺ - CHO), 406 (7, M⁺ - CF₃), 378 (4, M⁺ - CO - CF₃), 377 (7, M⁺ - CHO - CF₃), 306 [10,

M⁺ - CF(CF₃)₂], 69 (43, CF₃), and 68 (9, C₄H₄O); ν_{max} (liquid film) 1 605 (m, HC=CH), 1 645 (w, HC=CH), and 1 715 cm⁻¹ [w, (CF₃)₂CFC=CF] {Found [mixture of (21), (22), and (23)] C, 32.6; H, 0.9; F, 60.3; N, 3.3%; C₁₃H₄F₁₅NO requires C, 32.8; H, 0.8; F, 60.0; N, 2.9%}.

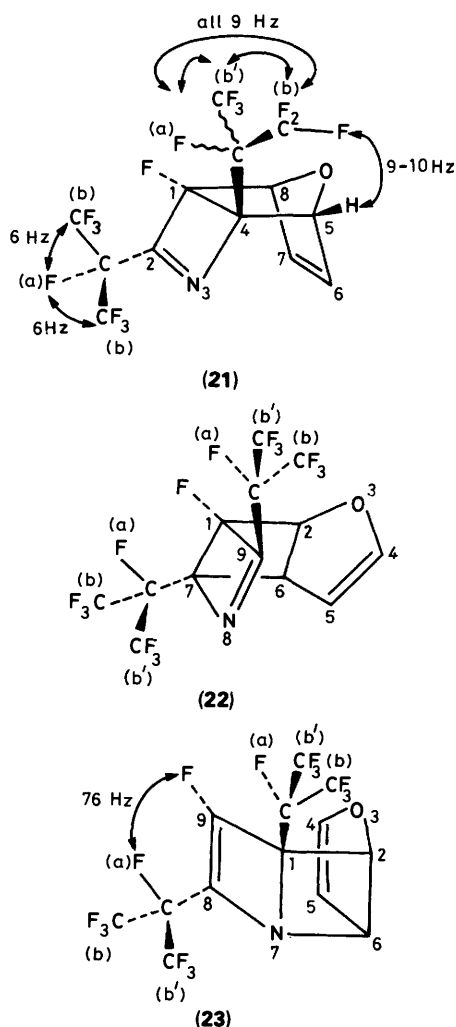
Results of similar reactions, done under different conditions are shown in Table 2.

Blank (control) experiment. An identical quartz tube containing the triazine (15), solvent, and furan, in the same quantities as [B(i)] was warmed (40 °C, 15 h) without irradiation. Analysis of the contents in a similar manner revealed that no reaction had taken place, the composition of the solution in the tube remaining unchanged.

(4) *Conversion of a Mixture of endo-1-Fluoro-2,4-diheptafluoroisopropyl-9-oxa-3-azatricyclo[4.2.1^{5,8,0}]octa-2,6-diene (21) and endo-1-Fluoro-7,9-diheptafluoroisopropyl-3-oxa-8-azatricyclo[5.2.0.0^{2,6}]nona-4,8-diene (22) into endo-9-Fluoro-1,8-diheptafluoroisopropyl-3-oxa-7-azatricyclo[5.2.0.0^{2,6}]nona-4,8-diene (23).*—Passage of (21) and (22) down a GLC column. A mixture of (21) and (22) (0.3 g, 0.63 mmol [ratio (21):(22):2.1] was passed through a preparative GLC column (column F) at 160 °C, the material isolated being found to consist of a single product (capillary GLC) identified as endo-9-fluoro-1,8-diheptafluoroisopropyl-3-oxa-7-azatricyclo[5.2.0.0^{2,6}]nona-4,8-diene (23), a colourless liquid (0.28 g, 93%).

Thermolysis (21) and (22) at 160 °C. A mixture of (21) and (22) (0.3 g, 0.63 mmol), in a Pyrex tube, was heated at 160 °C for 15 h. Analysis of the product (capillary GLC-MS) revealed a complex mixture of several components, all 1:1 adducts (*m/z* 475) including (23). This material was not investigated further.

(5) *Co-photolysis of Trifluoro-1,2,3-triazine (9) and Perfluoro-4,6-di-isopropyl-1,2,3-triazine (15).*—Trifluoro-1,2,3-triazine (9) (0.4 g, 3.0 mmol), perfluoro-4,6-di-isopropyl-1,2,3-triazine (0.3 g, 0.69 mmol), and 1,1,2-trichloro-1,2,2-trifluoroethane (5.0 g) in a quartz tube (20 ml) were irradiated (253.7 nm) for 24 h. The volatile product (0.24 g) isolated by evaporation of solvent at reduced pressure, was shown by GLC to contain three components. Separation and isolation by preparative GLC (column K) revealed them to be trifluoro-1,3,5-triazine (25)²⁵ (0.01 g), perfluoro-2,4-di-isopropylpyridine (27)²³ (0.17 g, 53%) and perfluoro-2,4,6,8-tetraisopropyl-1,5-diazatricyclo[4.2.0.0^{2,5}]-octa-3,7-diene (18) (0.03 g, 11%); characterisation was by com-



parison with authentic samples. The residue left in the quartz tube was a polymeric material with similar characteristics to that formed (11) on photolysis of trifluoro-1,2,3-triazine (9) alone.

(6) *Pyrolysis of Perfluoro-2,4,6,8-tetraisopropyl-1,5-diazatri-cyclo[4.2.0.0^{2.5}]octa-3,7-diene (18)*.—The diene (18) (0.2 g, 0.25 mmol) was sealed in a melting point tube, and heated (350 °C) for 1 h. The product was examined by ¹⁹F NMR spectroscopy (capillary method) and shown by GLC (column K) to contain two components perfluoro-2,4,6-tri-isopropylpyridine (19) (0.145 g, 98%),¹⁵ a colourless liquid, and perfluoroisobutyronitrile (14)¹² (quantitative) (by comparison with authentic samples).

(7) *Reaction of Perfluoro-2,4,6,8-tetraisopropyl-1,5-diazatri-cyclo[4.2.0.0^{2.5}]octa-3,7-diene (18) with anhydrous Caesium Fluoride: Formation of a Stable Carbanion (20)*.—The diene (18) (0.2 g, 0.25 mmol), dry diethyl ether (1 ml), dry sulpholane (0.5 ml), and anhydrous caesium fluoride (1.0 g, 6.6 mol) in an NMR tube (5 mm) were heated (100 °C, oil bath) under an atmosphere of dry nitrogen for 24 h. On cooling, and settling of solid, formation of *endo*-perfluoro-2,4,6,8-tetraisopropyl-1,5-diazatetracyclo[4.2.0.0^{2.5}.0^{3.8}]octan-4-ylcaesium (20) in virtually quantitative yield, was shown by ¹⁹F NMR spectroscopy. The anion (20) was stable to heating at 150 °C for several hours; δ_F 72.24 (3 F, m, 4b- or 4b'-F), 73.27 (6 F, s, 2b-F), 74.79 (3 F, m, J 8

Hz, 8b- or 8b'-F), 75.15 (3 F, m, J 8 Hz, 8b'- or 8b-F), 75.54 (3 F, m, J 7.5 Hz, 6b- or 6b'-F), 75.52 (3 F, m, J 7.5 Hz, 6b' or 6b-F), 76.72 (3 F, s, 4b'- or 4b-F), 88.51 (1 F, d, J 214.5 Hz, 7a-F), 95.97 (1 F, d, J 214.5 Hz, 7b-F), 157.10 (1 F, s, 3-F), 173.09 (1 F, m, J 9 Hz, 4a-F), 177.67 (1 F, br s, 8a-F), 188.02 (1 F, br s, 6a-F), and -187.07 (1 F, s, 2a-F); δ_{CS} 2.60 (s).

Reaction of Perfluoro-2,4,6,8-tetraisopropyl-1,5-diazatetracyclo[4.2.0.0^{2.5}.0^{3.8}]octan-4-ylcaesium (20) with Chlorine.—The NMR solution of (20) mentioned above was treated with a gentle stream of dry chlorine gas for *ca.* 10 min at room temperature to give a white precipitate and fading of the deep red colour of the solution. Filtration of the solution through several thicknesses of tissue paper, to remove residual caesium salts, gave a straw coloured solution. The product *endo*-perfluoro-4-chloro-2,4,6,8-tetraisopropyl-1,5-diazatetracyclo[4.2.0.0^{2.5}.0^{3.8}]octane (20a) (0.16 g, 75%) as a mixture of 2 isomers in the ratio of 1.7:1; *m/z* (%) 664 [14, *M*⁺ - Cl - CF(CF₃)₂, 69 (100, CF₃)]; δ_F 72.39, 72.49, 73.19, 73.21, 74.40, 75.06, 75.97, and 76.93 (24 F, all unresolved multiplets, 2b-, 4b-, 6b-, 8b-F both isomers); plus isomers (a) (major) 92.90 (1 F, d, J 247 Hz, 7a- or 7b-F), 94.20 (1 F, d, J 247 Hz, 7b- or 7a-F), 151.48 (1 F, s, 3-F), 178.35, 179.34, 180.65, and 187.36 (4 F, all singlets, 2a-, 4a-, 6a-, 8a-F); isomer (b) (minor) 89.30 (1 F, d, J 201 Hz, 7a- or 7b-F), 92.57 (1 F, d, J 201 Hz, 7b- or 7a-F), 174.95, 180.65, 183.26, and 187.12 (5 F, all singlets, 2a-, 3-, 4a-, 6a-, 8a-F).

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