

POLYHALOGENOHETEROCYCLIC COMPOUNDS - 38.
SYNTHESIS OF TRIFLUORO-1,2,3-TRIAZINE AND PERFLUOROISOPROPYL
DERIVATIVES¹

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Abstract: Reaction of trichloro-1,2,3-triazine (1) with potassium fluoride at elevated temperatures gives trifluoro-1,2,3-triazine (4) and corresponding chlorofluoro derivatives. Introduction of perfluoroisopropyl groups occurs, using fluoride ion and hexafluoropropene. A novel product (7) is described that arises from nucleophilic attack of perfluoroisopropyl anion on ring nitrogen in an intermediate triazine derivative.

Throughout this series of papers¹ we have been describing the synthesis and subsequent chemistry of members of a whole new class of perfluorinated heterocyclic systems and here we target the 1,2,3-triazine system. Perfluoro-1,3,5-triazine² has been known for some time, and perfluorinated derivatives of the -1,2,4-triazine system were synthesised more recently.^{3,4} However, fluorinated derivatives of the fascinating 1,2,3-system have not previously been described and, indeed, this system is somewhat underexplored⁵ viz. 1,2,3-triazine itself has been characterised comparatively recently.⁶ Nevertheless, Gompper and co-workers⁷ have reported a synthesis of trichloro-1,2,3-triazine and we now describe the synthesis of fluorinated derivatives, based on this starting material.

Trichloro-1,2,3-triazine is reactive towards nucleophilic aromatic substitution and therefore displacement of chloride by fluoride-ion is, in principle, a favourable approach to the synthesis of trifluoro-1,2,3-triazine. In this laboratory, we have previously synthesised a number of activated fluorinated heterocyclic systems using this approach; a very simple methodology that we developed involves heating the perchloro compound with anhydrous potassium fluoride in an autoclave or sealed tube and the corresponding perfluoro compound is subsequently distilled from the hot autoclave. However, this approach was not successful for the 1,2,3-triazine system because only limited fluorination occurred at 180°C (Table 1) and above this temperature extensive decomposition occurs.

Use of metal fluoride in an aprotic solvent is also a well established procedure but use of potassium fluoride and sulpholan gave limited conversions of trichloro-1,2,3-triazine under a variety of conditions. The most successful approach, so far, has been the use of potassium fluoride at higher temperatures but using short contact times; the procedure involved passing (1), by vacuum transfer, through a hot tube containing potassium fluoride. Higher yields of trifluoro-1,2,3-triazine (4) were obtained by a two-step process where products of initial

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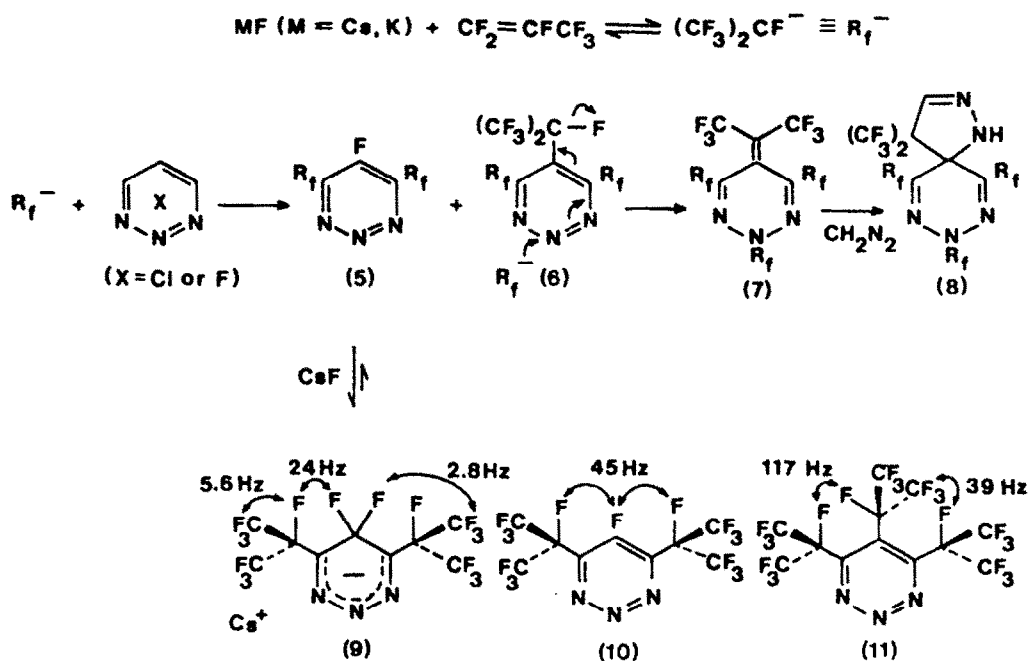
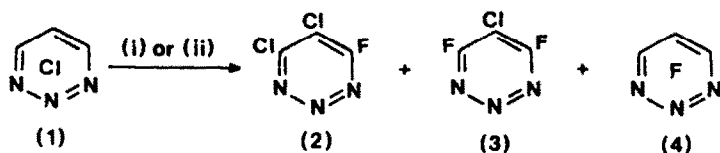
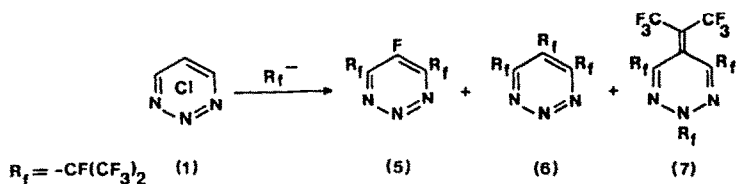


Table 1. Fluorination of Trichloro-1,2,3-triazine



	Products Yield (%)			
	<u>temperature ($^{\circ}\text{C}$)</u>	<u>(2)</u>	<u>(3)</u>	<u>(4)</u>
(i) KF, carius tube, 10^{-2} mm, 18 h.	150	49	11	-
	180	9	58	-
	200	0	37	-
(ii) KF, vacuum transfer 10^{-2} mm	a) 500 (1 cycle)	47	40	3
	a) 500 (4 cycles)	-	65	18
	a) 500 b) 600	-	15	69
	a) 450 b) 700	-	4	55
	a) 450 b) 600	-	18	65

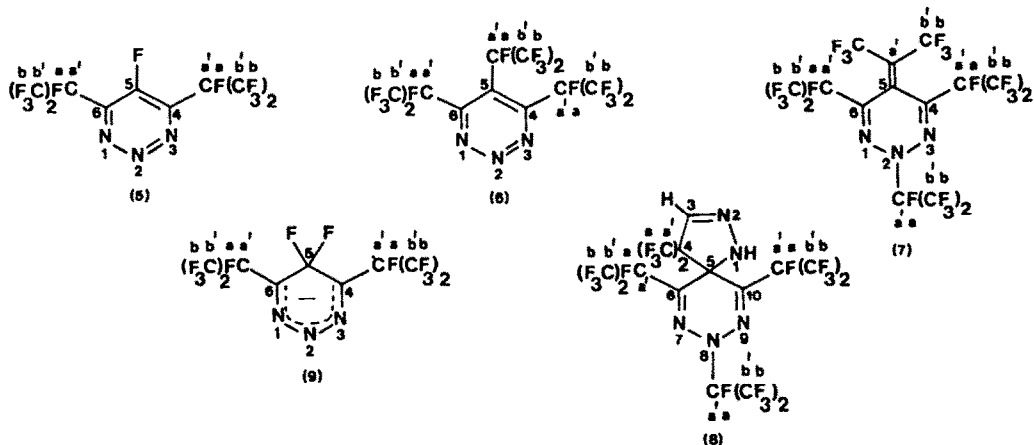
Table 2. Perfluoroalkylation of trichloro-1,2,3-triazine (1), reaction conditions and results



(1)	Metal fluoride,	HFP consumed	Solvent(s)	Conditions	Products yield %			
g, mmol	g, (mmol)	g, (equivalents)	ml		(5)	(6)	(7)	
A)								
a)	0.55, 3	KF, 1.2, (21)	3.0, (6.9)	tetraglyme 10	25°C, 7d	28	11	2
b)	0.55, 3	CsF, 2.7, (18)	3.0, (6.9)	tetraglyme 10		25	19	5
c)	0.55, 3	CsF, 2.7, (18)	3.0, (6.9)	tetraglyme 10	25°C, 2d	-	-	44
d)	0.55, 3	KF, 1.2 (21)	2.1 (4.7)	sulpholan 10	60°C, 1d	7	17	2 ^{††}
					25°C, 2d			
e)	2.75, 15	KF, 6, (105)	4.2 (1.9)	sulpholan 50	25°C, 18h	17	22	trace ^{††}
f)	2.4, 13	CsF, 12, (79)	4.6 (2.3)	sulpholan 30	25°C, 3d	47	6	3
g)	4.0, 22	CsF, 22, (145)	10.4 (3.0)	sulpholan 50	25°C, 2d	39	13	8
h)	1.65, 9	CsF, 8.1, (53)	8.5 (6.5)	sulpholan 30	25°C, 1d	6	7	40
B)								
(i)	1.5g, 8	KF, 3.6 (63)	-	sulpholan 20	25°C, 1d	48	3	2
				ether [†] 30				
(ii)		CsF, 3.5, (23)	2.4 (2.0)	sulpholan 20	25°C 1d			
				ether [†] 30				

[†] ether ≡ diethyl ether

^{††} in addition d) gave 6% and e) 8% of a compound of molecular formula C₆F₉N₃; m/z 285 (M⁺, 10%), 257 (M⁺-N₂, 9%), thought to be perfluoro-4-isopropyl-1,2,3-triazine, which has not been characterised



fluorination were recycled at a higher temperature.

Part of our interest in the 1,2,3-triazine system arises from their potential use as sources of azetes and perfluoroalkyl derivatives are especially interesting because of the unusual stabilising influence of perfluoroalkyl groups on small ring systems.⁹ For example, a range of remarkably stable valence isomers of aromatic systems has now been described.^{8,10} We have previously developed a polyfluoroalkylation procedure¹¹ which involves generation of perfluoroalkyl anions from a perfluorinated alkene in the presence of caesium- or potassium-fluoride, in aprotic media and the resultant anions then displace fluoride ions from appropriately reactive fluorinated aromatic systems. Trichloro-1,2,3-triazine is sufficiently reactive, however, to allow the fluorination and perfluoroalkylation procedure to be carried out simultaneously and compounds isolated from this procedure are shown in the Reaction Scheme.

At least partial fluorination of trichloro-1,2,3-triazine (1) must occur before subsequent displacement of fluoride ion by perfluoroalkyl groups and then any remaining chlorine will be more rapidly displaced, since perfluoroalkyl groups are strongly activating towards nucleophilic aromatic substitution. Products (5)-(7) were obtained using tetraglyme or sulpholan with potassium- or caesium-fluoride at room temperature but at higher temperatures (7) was the only product. Indeed, in a separate experiment, it was shown that a mixture of (5) and (6) is quantitatively converted to (7) at 60°C. Solubility of trichloro-1,2,3-triazine (1) in tetraglyme or sulpholan is quite low whereas it is extremely soluble in diethylether and we have found, therefore, that a co-solvent is extremely effective. Indeed, use of diethylether led to advantages of reproducibility, reduction of reaction times, and we also found that reactions were much more reliably scaled up using this co-solvent. Results which illustrate these points are contained in the experimental section.

Formation of a perfluorodialkyl derivative (5) by attack para to nitrogen is understandable because this orientation arises from the considerable activating influence of ring nitrogen but the further ready substitution to give (6) was rather surprising considering the significant steric effects anticipated for these perfluoroalkyl groups. However, the F-19 n.m.r. spectrum shows that the preferred conformation of the perfluoroisopropyl groups in (5) minimises the effect at the 5-position by having the trifluoromethyl groups flanking the adjacent ring nitrogen (10). Crowding is still significant in (6) because the F-19 n.m.r. spectrum demonstrates restricted rotation, making perfluoroisopropyl groups at the 4- and 6-positions non-equivalent (11). The most remarkable and unique feature of this reaction, however, is the isolation of a product (7) which arises from attack by a fourth equivalent of perfluoroalkyl anion. The process obviously involves a form of nucleophilic attack on ring nitrogen, which is a very rare process in an aromatic ring, although examples involving 1,2,3-triazines have been reported previously.^{12,13} Further investigations and extensions of this process will be described in separate publications.¹⁴

The structure of (7) follows partly from the F-19 n.m.r. spectrum and, conspicuously, the number of "tertiary" fluorines in relation to trifluoromethyl groups. Furthermore, the fluorine chemical shift of trifluoromethyl is quite diagnostic in distinguishing between trifluoromethyl, as part of $(CF_3)_2CF$, which normally occurs at -70 to -80 ppm, and a $CF_3-C=C$ location with a characteristic fluorine chemical shift of ca. -60 ppm. Experimental confirmation also follows from reaction with diazomethane; rapid reaction occurred and the Δ^2 pyrazoline (8) was formed. In previous work¹⁵ we have shown that fluorinated alkenes with perfluoroalkyl groups attached to the double bond are extremely reactive towards diazomethane, giving the Δ^2 pyrazolines and the formation of (8) is clearly consistent with these observations.

The perfluorodialkyl derivative (5) is extremely reactive towards nucleophiles and, in the presence of caesium fluoride in sulpholan, forms an observable σ -complex (9), analogous to complexes formed previously for trifluoro-1,3,5-triazine.¹⁶ Remarkably well resolved coupling was observed, for the caesium salt, between difluoromethylene and adjacent perfluoroisopropyl groups. No analogous observable complex could be generated using potassium fluoride but, using $(\text{Me}_2\text{N})_3\text{S}^+[\text{Me}_3\text{SiF}_2]^-$ ¹⁷ in acetonitrile, an analogous complex could be generated but not with the well-defined coupling shown by (9). This implies a less-stable complex, with some fluoride-ion exchange occurring. The complex (9) could also be generated in acetonitrile solvent and this retained at least some of the fine-structure, also implying that the complex (9) is more stable than the analogous complex associated with the TMS cation $(\text{Me}_2\text{N})_3\text{S}^+$.¹⁷ This is consistent with our observations involving perfluoroalkyl anions which we have discussed earlier.¹⁸

The formation of a relatively stable anion (9) has preparative significance because we can now account for the fact that reaction products contain a greater proportion of the perfluorodialkyl derivative (5), using caesium fluoride, than in analogous experiments using potassium fluoride which led to further substitution. We have also exploited this finding in developing a two-step procedure for the synthesis of perfluoroalkyl derivatives: the first stage involves reaction of trichloro-1,2,3-triazine (1) with potassium fluoride, to give chlorofluoro-1,2,3-triazene derivatives, which are then used for the second stage. The use of potassium fluoride for the first stage avoids formation of complexes with the fluorinated triazines. However, use of caesium fluoride for the subsequent reaction of the chlorofluorotriazines in the polyfluoroalkylation step deliberately encourages the formation of (9) and, consequently, increases the proportion of (5) in the ultimate product. The complex (9) is labile on heating, which allows the isolation of (5).

Fascinating chemistry arising from photolysis and pyrolysis of these triazine derivatives will be described in future publications.¹⁹

EXPERIMENTAL

Spectroscopic data were obtained using the following spectrometers: U.V., Pye Unicam S.P. 800; Mass, A.E.I. MS9, V.G. Micromass 12B linked to a Pye 104 gas chromatograph, or a VG-7070E instrument fitted with a Hewlett Packard 5790A capillary gas chromatograph; n.m.r., Varian A56/60D, Bruker HX90E, Bruker WH360 and Bruker AC-250. Chemical shifts are quoted as positive in p.p.m. downfield from tetramethyl silane (¹H, ¹³C) and nitromethane (¹⁵N), and as negative in p.p.m. upfield from fluorotrichloromethane (¹⁹F). Analytical g.l.c. was carried out on a Varian Aerograph 920 or Pye 104 gas chromatograph using columns packed with 20% 'Krytox' fluid on Chromosorb W (Column "K"), 20% 'Fomblin' fluid on Chromosorb P (Column "F") and 20% di-isodecylphthalate on Chromosorb P (Column "A"); and on a Hewlett Packard HP 5890-A capillary gas chromatograph. Preparative scale g.l.c. was performed on a Varian Aerograph 920 using Columns "K", "F" and "A". Caesium and potassium fluoride were dried by heating under high vacuum, with periodic grinding in a glove box (CSF). Anhydrous ether and tetraglyme were stored over sodium wire, and sulpholan was distilled at reduced pressure and stored over molecular sieves.

Trichloro-1,2,3-triazine (1). Crude trichloro-1,2,3-triazine (1) was prepared according to Gompper and Schonafinger⁷ and further purified by Soxhlet extraction with diethyl ether (x 2) to remove insoluble material (azide), recrystallisation from diethyl ether, then sublimation under high vacuum (10^{-2} - 10^{-2} mm).

Fluorination of Trichloro-1,2,3-triazine (1).

(i) Solid phase fluorination. The general procedure is illustrated by a representative example. A Carius tube (30 ml) containing trichloro-1,2,3-triazine (1) (1.5 g, 8.1 mmol) and dried potassium fluoride (3.3 g, 57 mmol), sealed under vacuum (10^{-2} mm) was heated at 180°C for 18 h. The product, isolated by vacuum transference, was shown by g.l.c. (Column "A") to contain 4,5-dichloro-6-fluoro-1,2,3-triazine (2) (0.11 g, 9%); m/z 171/169/167 (M^+ , 3/7/9%), 143/141/139 (M^+-N_2 , 2/15/21%), 134/132 (M^+-Cl , 7/23%); $\delta_p(\text{CDCl}_3)$ -79.5 (1F,s,F-6), and

5-Chloro-4,6-difluoro-1,2,3-triazine (3) (0.72 g, 58%), as white crystals m.p. 43-46°C; (found: C, 23.7; N, 27.8% $C_3ClF_2N_3$ requires: C, 23.8; N, 27.7%); m/z 153/151 (M^+ , 5, 15%), 125/123 (M^+-N_2 , 4/13%), 80/78 (17/58%), 69 (12); δ_F ($CDCl_3$) -80.0 (2F, s, F-4,6); δ_C ($CDCl_3$) 108.0 (t, J 26 Hz, C-5), 164.9 (d, J 265 Hz, C-4,6), along with a small amount of trichloroacrylonitrile (by comparison with an authentic sample).³ The results of experiments conducted at 150° and 200°C are also shown in Table 1(i).

(ii) Vapour phase fluorination (with Peter Hoare). The general procedure is illustrated by a representative example.

Preparation of a potassium fluoride bed.⁴ Potassium fluoride, dried at 200°C, was placed in a silica pyrolysis tube (18 mm i.d. x 300 mm) which had a glass rod (4 mm d.) lying along its central axis. The tube was heated in a furnace (250°C) for 2 h., and after the rod had been carefully removed to leave a small channel along the axis, dried at 600°C for 3 h. under high vacuum (10^{-1} - 10^{-3} mm).

a) Single step procedure. Trichloro-1,2,3-triazine (1) (5 g, 27 mmol) was sublimed at 60-80°C under high vacuum (10^{-2} mm), into the pyrolysis tube (maintained at 500°C), over a period of 2 h. Products were collected in a cold trap attached to the other end of the tube, and were isolated by preparative g.l.c. (Column "A") to give 4,5-dichloro-6-fluoro-1,2,3-triazine (2) (2.1 g, 47%), 5-chloro-4,6-difluoro-1,2,3-triazine (3) (1.6 g, 40%), and 4,5,6-trifluoro-1,2,3-triazine (4) (0.1 g, 3%) as a colourless liquid; (found C, 26.7; F, 42.6; N, 31.1% $C_3F_3N_3$ requires: C, 26.7; F, 42.2; N, 31.1%); λ_{max} 231 nm (ϵ_m 2100); δ_F ($CDCl_3$) -96.0 (2F, d J 23 Hz, F-4,6), -166 (1F, t J 23 Hz, F-5); δ_C ($CDCl_3$) 132.8 (d of t, J 298, 19 Hz, C-5), 157.8 (d, J 265 Hz, C-4,6); m/z 135 (M^+ , 12%), 107 (M^+-N_2 , 39), 62 (83).

b) Multiple step procedure. Multiple step fluorination was accomplished by passage of the products from an initial fluorination over the potassium fluoride bed at (in general) a higher temperature. Thus the product obtained in a) above was transferred into the fluorination tube (maintained at 600°C) over 1 h. The final product contained 4-Chloro-5,6-difluoro-1,2,3-triazine (3) (0.63 g, 15%) and trifluoro-1,2,3-triazine (4) (2.52 g, 69%). The results of stepwise fluorination at different temperatures are summarised in Table 1(ii).

Perfluoroalkylation of Trichloro-1,2,3-triazine (1). The general procedure is illustrated by a representative example.

A) Single step reaction. Dry, powdered caesium fluoride (22 g, 145 mmol) was placed in a flame dried 250 ml 3-necked flask, and heated at 150°C for 1 h. under high vacuum (10^{-2} - 10^{-3} mm). On cooling an atmosphere of dry nitrogen was introduced and, against a flow of nitrogen, anhydrous sulpholan (50 ml), diethyl ether (100 ml), and trichloro-1,2,3-triazine (1) (4.0 g, 22 mmol), was added along with a stirrer bar. A bladder containing hexafluoropropene (10.4 g, 69 mmol, 3 equiv.) was attached, the flask and contents cooled in liquid air, and evacuated (10^{-2} - 10^{-3} mm). The flask and contents were allowed to warm up to room temperature, hexafluoropropene was admitted in one portion from the bladder, and the mixture was stirred at 25°C for 2 days (or until the gas bladder had deflated). An atmosphere of dry nitrogen was introduced, ether was removed by distillation, and volatile products isolated by vacuum transference at up to 150°C (10^{-2} mm). Analysis and separation of products by g.l.c. (Columns "K" or "F") gave:

(i) Perfluoro-4,6-di-isopropyl-1,2,3-triazine (5) (3.69 g, 39%) as colourless crystals m.p. 52-53°C; (found: C, 24.5; F, 65.5; N, 10.0% $C_9F_{13}N_3$ requires: C, 24.8; F, 65.5; N, 9.7%); λ_{max} 206 nm (ϵ_m 1700); δ_F ($CDCl_3$) -75.5 (12F, t, J 12 Hz, F-4b,6b), -124.8 (1F, t of sept, J 45.4; 5.6 Hz, F-5), -186.3 (2F, d of sept, J 45.4; 5.6 Hz, F-4a,6a); δ_C ($CDCl_3$) 91.1 (d of sept, J 214; 35 Hz, C-4a',6a'), 119.3 (q of d, J 289; 27 Hz, C-4b',4b'), 141.6 (d, J 24 Hz, C-4,6), 154.6 (d, J 315 Hz, C-5); m/z 435 (M^+ , 1%), 407 (M^+-N_2 , 26), 338 (M^+-N_2 -CF₃, 10), 266 (M^+ -CF(CF₃)₂, 37).

(ii) Perfluoro-4,5,6-tri-isopropyl-1,2,3-triazine (6) (1.58 g, 13%) as a yellow liquid b.p. 163-165°C; (found: C, 24.7; F, 67.9; N, 7.5% $C_{12}F_{21}N_3$ requires: C, 24.6; F, 68.2; N, 7.2%); λ_{max} 231 nm (ϵ_m 2300); δ_F ($CDCl_3$) -72.4 (6F, d, J 39 Hz, F-5b), -74.5 (6F, d of d, J 17.5; 3.9 Hz, F-4b), -75.3 (6F, s, F-6b), -154.7 (1F, d of sept, J 117; 4 Hz, F-5a), -180.3 (1F, d of sept, J 117; 3.9 Hz, F-4a), -184.6 (1F, sept, J 39 Hz, F-6a); δ_C ((CD_3)₂CO) 148.1 (d, J 27.9 Hz, C-6), 145.5 (d of d, J 29.3; 2.8 Hz, C-4), 119.0 (q of d, J 288.3; 27.8 Hz, C-4b',6b'), 118.9 (q of d, J 289.2; 26.5 Hz, C-5b'), 118.0 (d, J 30.3 Hz, C-5), 93.8 (d of

sept, J 175.4; 36.5 Hz, C-5a'), 92.8 (d of sept, J 217; 34 Hz, C-4a',6a'); m/z 585 (M^+ , 0.5%), 557 (M^+N_2 , 2).

(iii) Perfluoro-2,4,6-tri-isopropyl-5-isopropylidene-1,2,3-triaza-cyclohexa-3,6-diene (7)

(1.28 g, 8.0%) as a yellow liquid b.p. 195-197°C; (found: C, 24.6; F, 70.1; N, 5.8% $C_{15}F_{27}N_3$ requires: C, 24.5; F, 69.8; N, 5.7%); λ_{max} 288 nm (ϵ_m 3700); δ_F (neat, 40°C) -61.3 (6F, d, J 39.5 Hz, F-5b), -72.9 (6F, S, F-4b or -6b), -77.7 (6F, S, F-2b), -78.2 (6F, S, F-6b or -4b), -153.4 (1F, S, F-2a), -177.6 (2F, q, J 39.5 Hz, F-4a,4b); δ_F (neat, above 70°C) -61.4 (6F, d, J 39.5 Hz, F-5b), -75.4 (12F, S, F-4b,6b), -77.9 (6F, S, F-2b), -153.0 (1F, S, F-2a), -176.7 (2F, q, J 39.5 Hz, F-4a,4b); δ_C ($(CD_3)_2CO$) 125.5 (d, 36.9 Hz, C-4,6), 122.3 (sept, J 34.2 Hz, C-5a'), 118.9 (q of d, J 288.4; 26.1 Hz, C-4b',6b'), 118.86 (q, J 279.2 Hz, C-5b'), 118.2 (q of d, J 289.3; 24.4 Hz, C-2b'), 117.8 (S, C-5), 97.2 (d of sept, J 236.2; 35.9 Hz, C-2a'), 92.9 (d of sept, J 216.6; 35.3 Hz, C-4a',6a'); δ_N ($CF_2ClCFCl_2$)/($(CD_3)_2CO$) -46.4 (S, N-1,3), 40.2 (d, J 14 Hz, N-2); m/z 735 (M^+ , 50%), 716 (M^+F , 29), 666 (M^+CF_3 , 12). Details for a series of experiments are given in Table 2a-h, involving variation of metal fluoride, solvent, quantity of hexafluoropropene, reaction time and temperature.

B) Two stage reaction (with Peter Hoare). Two stage perfluoroalkylation was accomplished by initial reaction of trichloro-1,2,3-triazine (1.5 g, 8 mmol) with potassium fluoride (3.6 g, 63 mmol) in diethylether/sulpholane co-solvent (30/20 ml), for one day at 25°C, followed by vacuum transference of the ether, fluorocarbon intermediates and some sulpholane (ca. 5 ml). More sulpholane (25 ml) was added to the ether/sulpholane/fluorocarbon solution, which was then subject to perfluoroalkylation conditions with hexafluoropropene (2.4 g, 2.0 equivalents) in the presence of caesium fluoride (3.5, 23 mmol). Reaction and subsequent work up was as described in A) above. The results of this experiment are given in Table 2i.

Reaction of Perfluoro-2,4,6-tri-isopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (7) with diazomethane

Perfluoro-2,4,6-tri-isopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (7) (0.5 g, 0.68 mmol) and diazomethane diethylether solution (5 ml, ca. 2.4 mmol) were placed in a round bottomed flask at room temperature, and set aside for 3 days. The product was shown by g.l.c. (Column "K") to have predominantly one component, and recrystallisation from diethyl ether gave 4,4-di-trifluoromethyl-4,8,10-tri-heptafluoroisopropyl-1,2,7,8,9-

penta-aza-spiro[4.5]deca-2,6,9-triene (8) (0.45 g, 85%) as yellow crystals m.p. 62-63°C; (found: C, 24.6; H, 0.0; F, 65.7; N, 8.9% $C_{16}H_2F_{27}N_5$ requires C, 24.7; H, 0.3; F, 66.0; N, 9.0%); λ_{max} 242 nm (ϵ_m 13200); δ_F ($CDCl_3$) -65.7 (6F, d, J 11.3 Hz, F-4a), -72.4 (6F, t, J 4.7 Hz, F-6b or -10b), -75.5 (6F, t, J 4.7 Hz, F-10b or -6b), -77.1 (6F, S, F-8b), -153.4 (1F, S, F-8a), -184.3 (2F, bs, F-6a, 8a); δ_C ($(CD_3)_2CO$) 126.1 (S, C-3), 125.8 (d, J 30 Hz, C-6,10), 120.3 (q, J 284.7 Hz, C-4a'), 119.1 (q of d, J 289.1; 25.9 Hz, C-8b'), 118.9 (q of d, J 288.2; 29.1 Hz, C-6b' or -10b'), 118.1 (q of d, J 289.6; 29.7 Hz, C-10b' or -6b'), 96.2 (d of sept, J 235.1; 35.5 Hz, C-8a'), 92.9 (d of sept, J 223.2; 33.1 Hz, C-6a',10a'), 76.2 (sept, J 27.7 Hz, C-4), 63.3 (S, C-5); δ_H ($(CD_3)_2CO$) 7.2 (1H, S, H-3a), 8.4 (1H, bs, H-1a); m/z 776 (M^+-1 , 0.6%), 775 ($M^+-2,4$), 773 (M^+-3 , 20), 756 (M^+-HF , 12).

Reaction of Perfluoro-4,6-di-isopropyl-1,2,3-triazine (5) with fluoride ion: Formation of a Stable Nitranion Perfluoro-5,5-difluoro-4,6-di-isopropyl-1,2,3-triazacyclohexa-3,6-diene-2-yl Nitranion (9)

a) With caesium fluoride in sulpholane and diethyl ether. A solution of perfluoro-4,6-di-isopropyl-1,2,3-triazine (5) (0.1 g, 0.23 mmol) in anhydrous diethyl ether (0.4 ml) was added to a 5 mm n.m.r. tube containing anhydrous sulpholane (1 ml) and dry caesium fluoride (0.35 g, 2.3 mmol). The mixture was shaken, a yellow-orange colour developed in both sulpholane and ether layers. δ_F -37.3 (2F, t of sept, J 24.2; 2.8 Hz, F-5), -75.7 (12F, t of d, J 24; 5.6 Hz, F-4b,6b), -189.6 (2F, t of sept, J 24, 5.6 Hz, F-4a,6a).

b) With caesium fluoride in acetonitrile. To a solution of perfluoro-4,6-di-isopropyl-1,2,3-triazine (5) (0.1 g, 0.23 mmol) in dry acetonitrile (1.4 ml) in a 5 mm n.m.r. tube, caesium fluoride (0.35 g, 2.3 mmol) was added, and the mixture shaken. A deep red-orange colour rapidly developed. δ_F -36.7 (2F, bt, J 24 Hz, F-5), -75.5 (12F, bs, F-4b,6b), -189.2 (2F, bs, F-4a,4b).

c) With TAS-F ($(Me_2N)_3S^+Me_3SiF_2^-$) in acetonitrile.¹⁸ To perfluoro-4,6-di-isopropyl-1,2,3-triazine (5) (0.2 g, 0.46 mmol) in a 5 mm n.m.r. tube, a solution of TAS-F (ca. 0.21 g, 0.78 mmol) in acetonitrile (1.4 ml) was added under a nitrogen atmosphere. All solid

dissolved immediately, and a deep yellow colour rapidly developed. δ_F -36.9 (~1F, bs, F-5 (exchanging)), -75.4 (12F, d, J 5.6 Hz, F-4b,6b), -188.7 (2F, bs, F-4a,4b).

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