

## Polyhalogenoheterocyclic Compounds. Part 39. Reactions of 4,5,6-Tris(perfluoroisopropyl)-1,2,3-triazine involving Nucleophilic Attack at Heterocyclic Nitrogen. X-Ray Crystal Structure of a Spiro Triazinium Zwitterion

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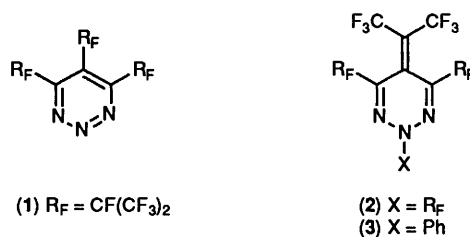
Reactions of 4,5,6-tris(perfluoroisopropyl)-1,2,3-triazine (**1**) with phenylmagnesium bromide and a range of electron-rich alkenes and dienes are described. Reactions result in addition onto the 1,2,3-triazine system by nucleophilic attack at N-2. Phenylmagnesium bromide and triazine (**1**) yield 2-phenyl-1,2,3-triazine derivative (**3**); reactions of (**1**) with dimethylbutadiene and isoprene yield the spirotriazinium zwitterion structures (**5a-c**). 2,3-Dimethylbut-2-ene and 2-methylbutene react with triazine (**1**) to give the *N*-substituted triazines (**9a**) and (**9b**), respectively. X-Ray crystal analysis reveals that the triazine ring of adduct (**5a**) adopts an eclipsed boat conformation.

As a continuation of our studies on fluorinated nitrogen heterocycles we have recently described the synthesis of the 1,2,3-triazine system substituted with fluorine and perfluoroisopropyl groups.<sup>1</sup> It is significant that the chemistry of this heterocyclic system is relatively underdeveloped; for example, the parent compound, 1,2,3-triazine, was characterised only comparatively recently.<sup>2</sup> Our interest in fluorinated 1,2,3-triazines stems from their potential as precursors to azetes<sup>3</sup> and from the opportunities this highly electron-deficient system affords for reactions with nucleophiles. Here we describe remarkable chemistry which derives from the fact that tris-(heptafluoroisopropyl)-1,2,3-triazine (**1**) undergoes nucleophilic attack *at nitrogen*.<sup>4</sup> For example, product (**2**) is formed in quantitative yield, from reaction of a mixture of (**1**) and 4,6-bis(perfluoroisopropyl)-5-fluoro-1,2,3-triazine and hexafluoropropene in the presence of caesium fluoride at 60 °C.<sup>1</sup> We now describe the reactions of compound (**1**) with a Grignard reagent and with electron-rich dienes and alkenes, all of which result in addition onto the 1,2,3-triazine system by nucleophilic attack at N-2.

Nucleophilic attack at heterocyclic nitrogen is an unusual process. Substituted oxaziridines react in this way with dimethylamine or methanol, with fragmentation of the heterocycle.<sup>5</sup> More recently, Storr and co-workers have shown that alkyl Grignard reagents react at N-2 of 4-substituted 1,2,3-benzotriazines to afford substituted benzindazoles.<sup>6</sup> Japanese workers have reported that Grignard reagents react at C-4 and C-5 of 1,2,3-triazine, but when the 4- and 6-positions are blocked, *viz.* 4,6-dimethyl-1,2,3-triazine, reaction is diverted to N-2 and a mixture of products is obtained resulting from nucleophilic attack at N-2 and C-4.<sup>7</sup>

### Results and Discussion

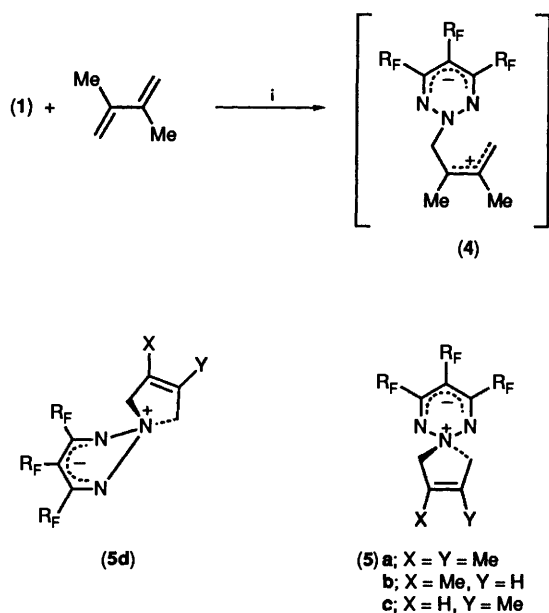
Reaction of triazine (**1**) with phenylmagnesium bromide (at 20 °C) or with phenyl-lithium (at -78 °C → 0 °C) yield the *N*-phenyl derivative (**3**). That attack occurred on nitrogen is clear from the <sup>19</sup>F NMR spectrum of product (**3**) which displays characteristic features of the perfluoroisopropylidene group, *viz.* δ<sub>F</sub> -60.3 ppm, [*cf.* compound (**2**), δ<sub>F</sub> -61.3 ppm].<sup>1</sup> We could not detect any products resulting from nucleophilic attack at carbon in triazine (**1**). Based on the precedent set by the Japanese work outlined earlier,<sup>7</sup> we might expect that com-



ound (**1**) would react exclusively at N-2 and the stabilising influence of perfluoroalkyl groups on negative charge is clearly the more influential effect in this system. It is noteworthy that we could not detect the formation of biphenyl in the reaction mixture; this argues against the involvement of phenyl radicals which would have resulted from a single electron transfer (SET) process such as that which we have observed previously with a fluorinated alkene,<sup>8</sup> and clearly favours a mechanism where the phenyl anion acts as a nucleophile attacking N-2 of triazine (**1**) followed by elimination of fluoride ion from the perfluoroisopropyl group at C-5. (We have further evidence against a SET process in that the conversion of (**1**) → (**2**) is not inhibited by the presence of oxygen.)

A large excess of 2,3-dimethylbutadiene reacted with compound (**1**) at 70 °C to yield a crystalline 1:1 adduct (70% yield). The <sup>13</sup>C NMR spectrum of the adduct clearly showed a highly symmetrical structure with two equivalent perfluoroisopropyl groups [presumably derived from those attached to C-4 and C-6 of triazine (**1**)]; the methyl groups were almost equivalent (δ<sub>C</sub> 10.8 and 11.1 ppm) while the two methylene groups were clearly inequivalent (δ<sub>C</sub> 74.0 and 83.7 ppm). The <sup>1</sup>H NMR spectrum of the adduct was consistent with these data, comprising singlets from two virtually equivalent methyl groups (δ<sub>H</sub> 1.69, 1.79) along with two inequivalent methylene singlets (δ<sub>H</sub> 4.24 and 4.83). The structure could not be deduced unambiguously from spectroscopic data, however, and an X-ray crystal structure determination showed that the adduct had the spiro structure (**5a**) (see below) the conformation of which may be represented by (**5d**). This structure is zwitterionic: the positive charge is localised on the spiro nitrogen, while the

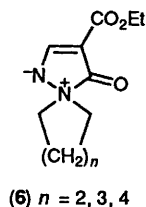
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**Scheme 1.** Reagents and conditions: i, 70 °C, 4 days.

negative charge can be delocalised over the remainder of the triazine ring. A noteworthy feature of the  $^{19}\text{F}$  NMR spectrum of compound (5a) is the non-equivalence of the  $\text{CF}_3$  groups within the perfluoroisopropyl groups at C-4 and C-5, while those of the perfluoroisopropyl group at C-6 are equivalent. This is consistent with the geared conformations (5b) and (5c), analogous to that observed in the solid state (see later), and suggests that the solution structure averages to a conformation approximating to (5d).

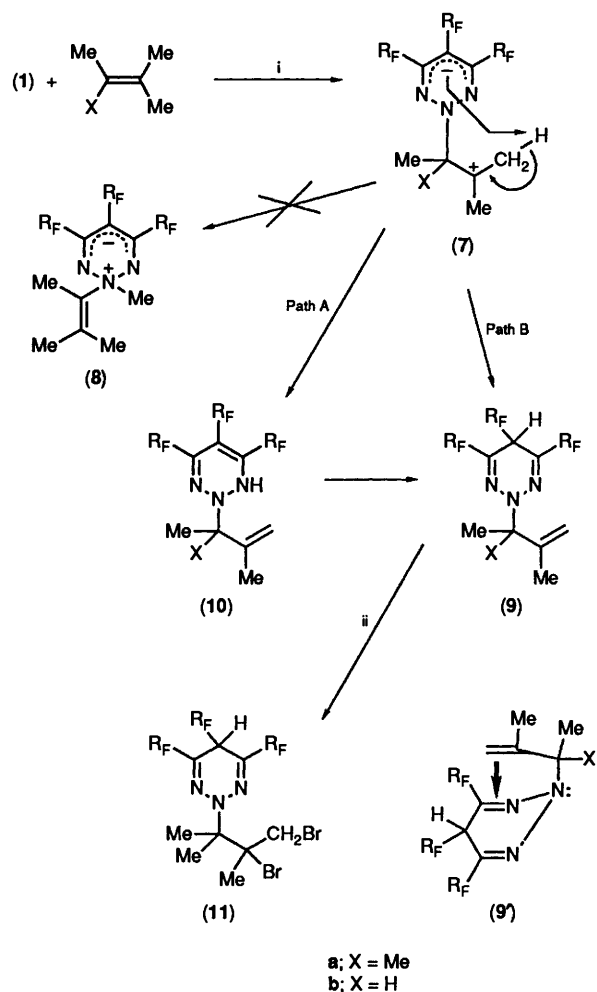
This fascinating product (5a) is the result of a formal cheletropic addition of the diene to N-2 of triazine (1). To our knowledge, this process is unprecedented in the chemistry of nitrogen heterocycles, although other spiro nitrogen heterocycles, which are also zwitterions, can be formed by totally different methods, e.g. spiropyrazolium zwitterions (6).<sup>9</sup>



It is interesting to note the analogy between the conversion of (1)  $\rightarrow$  (5a), and the well-known cheletropic addition of butadiene to sulphur dioxide. While a concerted mechanism for formation of adduct (5a) cannot be ruled out, it is more likely that a stepwise process occurs (Scheme 1). This would involve initial nucleophilic attack by the diene on N-2, to give intermediate zwitterion (4), which then cyclises to afford the spiro product (5a).

Reaction of isoprene with triazine (1) gave a yellow adduct, the structure of which followed from the close similarity of the IR, UV, and NMR spectra with those of adduct (5a). The two possible isomers (5b) and (5c) from isoprene addition were present in ca. 1:1 ratio as judged by  $^1\text{H}$  NMR data and the existence of these two isomers is more easily appreciated by considering the conformation (5d) which is derived from the solid state structure of (5a).

Reactions of substituted alkenes with triazine (1) have also been studied. 2,3-Dimethylbut-2-ene reacted with (1) to give a



**Scheme 2.** Reagents and conditions: i, 70 °C, 2 days; ii,  $\text{Br}_2$ ,  $\text{CCl}_4$ , reflux, 10 min.

1:1 adduct (96% yield) isolated as a green oil. We initially assigned the analogous structure (8) to this product,<sup>4</sup> which would be formed by methyl shift onto nitrogen, from an intermediate (7a), related to (4). However, the alternative adduct structure (9a) is the correct structure for the 2,3-dimethylbut-2-ene adduct. We became aware that structure (8) was inadequate following the reaction of the adduct with bromine. A singlet integrating for three protons at  $\delta_{\text{H}}$  4.80 which had previously been assigned to the  $\overset{+}{\text{N}}\text{Me}$  group of structure (8) was cleanly resolved in the brominated product into three singlets each of one proton intensity [ $\delta_{\text{H}}$  5.24 (br), 4.22, and 4.18]. This clearly required that a proton had been lost from a methyl group of intermediate (7a) and the adduct had either structure (9a) or (10a), instead of structure (8) (Scheme 2). At first sight, transfer of hydrogen to nitrogen of intermediate (7a) to yield (10a), which could occur *via* a favourable six-membered transition state, (Path A) might seem preferable to transfer of hydrogen to carbon to yield (9a) (Path B). However, we can confidently discount structure (10a) for the following reasons. Firstly, the NH proton of structure (10a) should be particularly labile to H/D exchange, but we can find no evidence from  $^1\text{H}$  NMR spectra that any exchange occurs in this adduct ( $\text{D}_2\text{O}/\text{CDCl}_3$  or  $\text{EtOD}/\text{CDCl}_3$ ). Secondly an NH absorption is not observed in the IR spectrum. Decisive evidence in favour of structure (9a) is provided by a combination of  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR data. The proton-coupled  $^{13}\text{C}$  NMR spectrum shows a

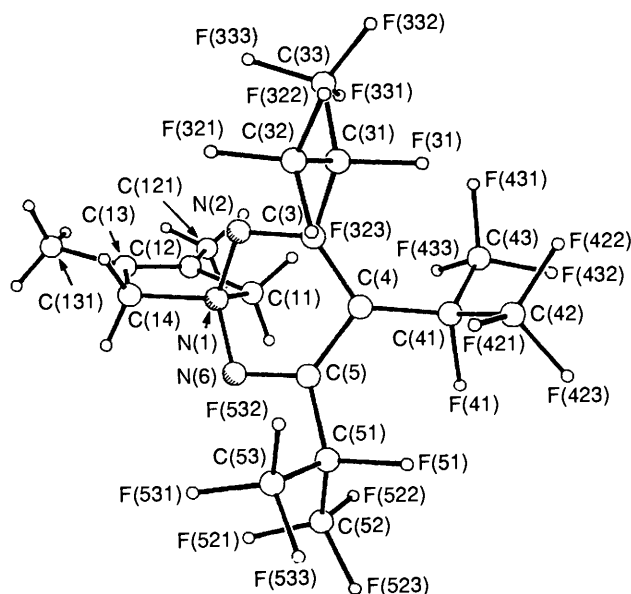


Figure. Structure of compound (5a) determined by X-ray crystallography.

Table 1. Interplanar angles for compound (5a).

Plane	Atoms
1	C(4), C(3), N(2), N(1)
2	C(4), C(5), N(6), N(1)
3	N(2), C(3), C(5), N(6)
4	N(6), N(1), N(2)
5	C(3), C(4), C(5)
Plane 1 $\wedge$ 2 = 136.6°	
Plane 3 $\wedge$ 4 = 131.0°	
Plane 3 $\wedge$ 5 = 159.9°	

doublet at  $\delta_C$  31.2 which can be assigned to C-5, and the  $^{19}\text{F}$  NMR spectrum shows coupling of a hydrogen to one of the tertiary fluorines ( $\delta_F -176.7$   $J_{5-H-F-5a}$ , 10 Hz). These data rule out structure (10a) for the product we isolate, although it is possible that (10a) is an intermediate in the formation of (9a) (Path A).

The three proton singlet of adduct (9a) at  $\delta_H$  4.80, which had initially misled us to structure (8), is the result of accidental equivalence of the two methylene protons and the hydrogen at C(5). The brominated product, described above, is, therefore, structure (11).

2-Methylbutene reacts with triazine (1) in a directly analogous manner, to yield the adduct (9b). The green colour of adducts (9a) and (9b) is possibly due to intramolecular charge-transfer from the electron-rich exocyclic double bond to the highly electron deficient triazine ring. A possible conformation for these molecules is shown by structure (9').

*X-Ray Crystal Structure of Compound (5a).*—The single crystal X-ray structure of compound (5a) is shown in the Figure.\* The triazine ring adopts an eclipsed boat conformation, which is more flattened at the highly sterically crowded C(4)-end of the ring. Interplanar angles are given in Table 1.

\* The numbering scheme of the Figure is used in discussion of the X-ray structure. Elsewhere in the text and experimental, the numbering scheme of structure (5a) is used.

† See 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans 1*, 1990 Issue 1, p. xvii.

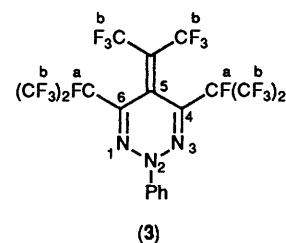
The least-squares best plane through the atoms of the five-membered ring [*viz.* N(1), C(11), C(12), C(13), and C(14)] makes an angle of 88.9° with plane number 4 [N(6), N(1), N(2)]. Chemically equivalent bonds throughout the structure are in reasonably close agreement, with the 'double'-bonds N(2)=C(3) [1.311(4) Å], N(6)=C(5) [1.299(5) Å], and C(12)=C(13) [1.323(5) Å] all remarkably short.

Bond angles at N(1) are within 4° of tetrahedral, opening to 113.2° at C(11)-N(1)-N(6) and closing to 106.1° at C(11)-N(1)-C(14). Angles at N(2) and N(6) are 110.3° and 110.9°, respectively, while at C(3) and C(5) they have opened to 124.8° and 124.1°, respectively. Bond angles at C(4) sum to 360.0° exactly, indicating planarity here. Expected trends in bond angles around the 5-membered ring are also observed (*viz.* decrease below 108° at  $sp^3$  hybridised atoms, increase at  $sp^2$  hybridised atoms and Me-Me repulsions). Bond lengths and bond angles for compound (5a) are available on request from the Cambridge Crystallographic Data Centre.†

## Experimental

Details of instrumentation have been given previously.<sup>1</sup>

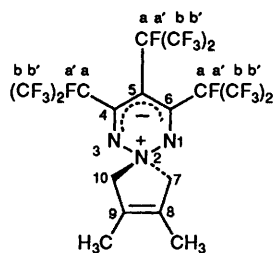
*Reaction of Perfluoro-4,5,6-triisopropyl-1,2,3-triazine (1) with Phenylmagnesium Bromide.*—Phenylmagnesium bromide ether solution (1 ml, 0.5M, 0.5 mmol) was added to triazine (1) (0.5 g, 0.85 mmol) in dry ether (5 ml) under nitrogen. The solution was stirred at 20 °C for 24 h. GLC analysis showed the presence of unchanged triazine (1) and a product which was isolated by vacuum transfer and identified as 4,6-bis-(heptafluoroisopropyl)-5-hexafluoroisopropylidene-2-phenyl-1,2,3-triazacyclohexa-3,6-diene (3) (0.25 g, 44%), a light brown viscous liquid (Found: C, 33.5; H, 0.9; F, 59.5; N, 6.2.  $C_{18}H_5F_{20}N_3$  requires C, 33.6; H, 0.8; F, 59.1; N, 6.5%)  $m/z$  643 ( $M^+$ , 24%), 624 (6), and 574 (4);  $\lambda_{max}$  204 ( $\epsilon_m$  14 000), 247 (5 600), 354 (12 300), and 498(sh) nm;  $\delta_H$ ( $CDCl_3$ ) 8.3–7.6 (m);  $\delta_F$ ( $CDCl_3$ ) –60.3 (6 F, d, F-5b,  $J_{5b,6a}$  37 Hz), –75.0 (12 F, s, F-4b and -6b), and –177.3 (2 F, F-4a and -6a, q,  $J_{4a,5b}$ ,  $J_{6a,5b}$  37 Hz).



*Reactions of Triazine (1) with Dienes and Electron-rich Alkenes. General Procedure.*—Appropriate quantities of triazine (1) and diene or alkene were placed in a Pyrex tube (*ca.* 50 ml) to which a Teflon vacuum tap (Rotoflo) was attached. The tube and contents were cooled (liquid air) while being evacuated ( $10^{-2}$  mmHg), the tap was then closed and the tube was allowed to warm to room temperature and then heated at 70 °C for several days. Products were isolated by evaporation of excess alkene at atmospheric or reduced pressure, followed by either crystallisation or distillation at reduced pressure ( $10^{-2}$  mmHg) of the residue. Product purity was monitored by capillary GC.

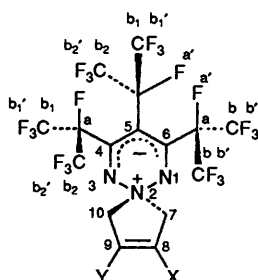
(a) *With 2,3-dimethylbutadiene.* Triazine (1) (0.6 g, 1.02 mmol) and 2,3-dimethylbutadiene (2.0 g, 24.4 mmol) were heated at 70 °C for 4 days. Recrystallisation of the crude product from light petroleum (b.p. 60–80 °C) gave adduct (5a) (0.48 g, 70%) as yellow crystals, m.p. 85–87 °C. (Found: C, 32.3; H, 1.6; F, 59.8; N, 6.0.  $C_{18}H_{10}F_{21}N_3$  requires C, 32.4; H, 1.5; F, 59.8; N,

6.3%)  $m/z$  667 ( $M^+$ , 1%), 648 (0.2), 598 (0.8), 497 (4), 82 (100), and 69 (40);  $\nu_{\max}$ (Nujol) 1570(s), 1440(m), 1365(w), 1300–1200 (br bands)  $\text{cm}^{-1}$ ;  $\lambda_{\max}$ (cyclohexane) 199.8 ( $\epsilon_m$  6 620), 263.8 (5 520), and 343 (3 640) nm;  $\delta_F$ ( $\text{CDCl}_3$ ) –67.9 (3 F, s, F-5b'), –73.0 (6 F, s, F-6b'), –75.7 and –76.2 (both 3 F, s, F-4b'), –77.6 (3 F, s, F-5b'), –151.5 (1 F, s, F-5a'), and –179.2 and –181.6 (both 1 F, s, F-4a', –6a');  $\delta_H$ ( $\text{CDCl}_3$ ) 4.83 and 4.24 (both 2 H, s, 10-H<sub>2</sub> and 7-H<sub>2</sub>), 1.79 and 1.69 (both 3 H, s, 8-H<sub>3</sub>, 9-H<sub>3</sub>);  $\delta_C$ ( $\text{CDCl}_3$ ) 155.9 (s, C-4 and C-6), 124.8 and 124.1 (both s, C-8 and C-9), 121.1 (q of d,  $J$  288.8, 29.2 Hz, C-5b), 119.9 (q of d,  $J$  287.5, 27.3 Hz, C-4b), 94.7 (d of sept,  $J$  218.2, 35.0 Hz, C-5a), 91.4 (d of sept,  $J$  245.0, 33.8 Hz, C-4a, –6a), 91.1 (d,  $J$  25 Hz, C(5) 83.7 and 74.0 (both s, C-7, C-10), 11.1 and 10.8 (both s, CH<sub>3</sub>).



(5a)

(b) *With isoprene.* Triazine (1) (0.6 g, 1.02 mmol) and isoprene (2.0 g, 29.4 mmol) were heated at 70 °C for 4 days. Micro-distillation yielded *products* (5b) and (5c) as an inseparable mixture of isomers, (0.5 g, 75%); yellow crystals, m.p. 60–63 °C (Found: C, 31.5; H, 1.1; F, 60.7; N, 6.5.  $\text{C}_{17}\text{H}_8\text{F}_{21}\text{N}_3$  requires C, 31.2; H, 1.2; F, 61.1; N, 6.4%)  $m/z$  653 ( $M^+$ , 28%), 634 (18), 584 (6), 484 (8), 69 (80), and 68 (100);  $\nu_{\max}$ (Nujol) 1568(s), 1439(m), 1365(m), 1300–1200(br)  $\text{cm}^{-1}$ ;  $\lambda_{\max}$ (cyclohexane) 200.0 ( $\epsilon_m$  6 800), 264.1 (5 610), 343 (3 660) nm;  $\delta_F$ ( $\text{CDCl}_3$ ) –68.0 (3 F, s, F-5b'), –73.4 (6 F, s, F-6b'), –75.4 and –76.1 (both 3 F, s, F-4b<sub>1</sub>' and –4b<sub>2</sub>'), –78.0 (3 F, s, F-5b<sub>2</sub>'), –151.8 (1 F, s, F-5a'), –179.3 and –181.7 (both 1 F, s, F-4a' and –6a');  $\delta_H$ ( $\text{CDCl}_3$ ) 1.80 (3 H, s, 8a-H<sub>3</sub>), 1.89 (3 H, s, 9b-H<sub>3</sub>), 4.23 (2 H, s, 7a-H<sub>2</sub>), 4.37 (2 H, s, 7b-H<sub>2</sub>), 4.82 (2 H, s, 10b-H<sub>2</sub>), 4.90 (2 H, m,  $J$  1.48 Hz, 10a-H<sub>2</sub>), 5.46 (1 H, m,  $J$  1.29 Hz, 8b-H), and 5.61 (1 H, m,  $J$  1.28 Hz, 9a-H).

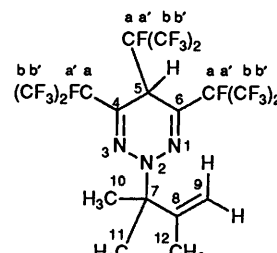


(5b) Y = H; X = Me

(5c) Y = Me; X = H

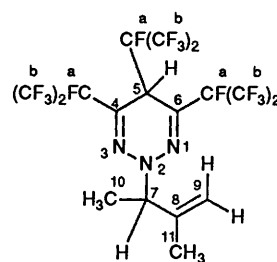
(c) *With 2,3-dimethylbut-2-ene.* Mixing of triazine (1) (0.4 g, 0.7 mmol) and 2,3-dimethylbut-2-ene (1.5 g, 17.9 mmol) resulted in initial formation of a deep red colour which was discharged on cooling. On warming to 20 °C and subsequent heating for 4 days at 70 °C, the red colouration reformed then changed to a deep green colour. Microdistillation afforded *product* (9a) as a green oil (0.44 g, 96%) (Found: C, 32.7; H, 1.6; F, 59.0; N, 6.5.  $\text{C}_{18}\text{H}_{12}\text{F}_{21}\text{N}_3$  requires C, 32.3; H, 1.8; F, 59.6; N, 6.3%)  $m/z$  669 ( $M^+$ , 0.4%), 628 (14), 500 [ $M^+$  – CF(CF<sub>3</sub>)<sub>2</sub>] (11), 84 (11), and 83 (100);  $\lambda_{\max}$  218 ( $\epsilon_m$  3 600), 247

8 200), 292 (6 200), and 398 (30) nm;  $\nu_{\max}$ (neat) 2 960(m), 1 635(w), 1 555(m), 1 455(m), 1 380(m), 1 330, and 1 100  $\text{cm}^{-1}$ ;  $\delta_F$ ( $\text{CDCl}_3$ ) –73.1 (6 F, s, F-4b' or –6b'), –75.3 (6 F, s, F-5b'), –77.4 (6 F, s, F-6b' or –4b'), –176.7 (1 F, d,  $J$  10 Hz, F-5a'), –180.9 (2 F, s, F-4a', –6a');  $\delta_H$ ( $\text{CDCl}_3$ ) 1.46 (3 H, s), 1.49 (3 H, s), 1.54 (3 H, s), 4.80 (3 H, m, CH<sub>2</sub>–C-9, H–C-5);  $\delta_C$ ( $\text{CDCl}_3$ ) (multiplicity is given for proton decoupled spectra followed by proton coupled spectra) 146.4 (s, s, C-8), 120.1 (q of d,  $J$  288, 24.6 Hz overlapping q of d,  $J$  288, 29.9 Hz, q of d overlapping q of d, C-4b, –5b, –6b), 117.9 (d of m,  $J$  37, 3 Hz, d of m, C-4, –6), 122.8 (s, t of q,  $J$  156.9, 5.8 Hz, C-9), 94–87 (overlapping sept of m, sept of m, C-4a, –5a, –6a), 72.4 (s, s, C-7), 31.2 (d,  $J$  25.6 Hz, dd,  $J$  10 Hz, C-5), 25.2 (s, q,  $J$  128.9 Hz, C-10, –11), 18.1 (s, q,  $J$  127.1 Hz, C-12).



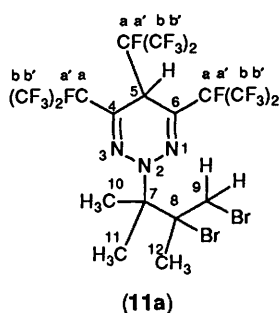
(9a)

(d) *With 2-methylbut-2-ene.* Triazine (1) (0.4 g, 0.7 mmol) and 2-methylbut-2-ene (2.0 g, 28.6 mmol) after being heated for 6 days at 70 °C gave a dark green solution. Microdistillation yielded *product* (9b) as a green oil (0.38 g, 85%). (Found: C, 30.8; H, 1.5; F, 61.0; N, 6.8.  $\text{C}_{17}\text{H}_{10}\text{F}_{21}\text{N}_3$  requires C, 31.1; H, 1.5; F, 60.9; N, 6.4%)  $m/z$  665 ( $M^+$ , 0.2%), 614(1), 487(7), 486(22), 70(36), and 69(100);  $\nu_{\max}$ (neat) 1 650(w), 1 557(m), 1 445(w), 1 375(m), and 1 330–1 060 (br bands)  $\text{cm}^{-1}$ ;  $\lambda_{\max}$ (cyclohexane) 244 ( $\epsilon_m$  5 960), 298 (5 200), and 404 (300) nm;  $\delta_F$ ( $\text{CDCl}_3$ ) –72.9 (6 F, s, F-4b or –6b), –75.2 (6 F, s, F-5b), –77.3 (6 F, d,  $J$  13.6 Hz, F-6b or –4b), –177.15 (1 F, d,  $J$  10 Hz, F-5a), –180.9 and –181.16 (both 1 F, s, F-4a, –6a);  $\delta_H$  1.48 (3 H, d,  $J$  6.9 Hz, 10-H<sub>3</sub>), 1.64 (3 H, s, 11-H<sub>3</sub>), 4.72 (1 H, q,  $J$  6.9 Hz, 7-H), 4.88 (1 H, br s, 5-H), and 4.98 (2 H, d,  $J$  5 Hz, 9-H<sub>2</sub>).



(9b)

*Reaction of Adduct (9a) with Bromine.*—A mixture of adduct (9a) 0.2 g, 0.3 mmol) and bromine (1.0 g, 6.2 mmol) was refluxed in carbon tetrachloride (5 ml) for 10 min. Evaporation of solvent left *product* (11) as a yellow oil (Found: C, 26.1; H, 1.4; N, 5.0.  $\text{C}_{18}\text{H}_{12}\text{Br}_2\text{F}_{21}\text{N}_3$  requires C, 26.1; H, 1.4; N, 5.1%)  $\lambda_{\max}$ (cyclohexane) 249.2 ( $\epsilon_m$  10 400), 283 (6 970), and 367 (790) nm;  $\nu_{\max}$ (neat) 2 960(w), 1 555(w), 1 445(w), 1 375(m), and 1 330–1 100 (str bands)  $\text{cm}^{-1}$ ;  $\delta_F$ ( $\text{CDCl}_3$ ) –73.4 (6 F, s, F-4b' or –6b'), –75.6 (6 F, s, F-5b'), –77.2 (6 F, s, F-4b' or –6b'), –177.7 (1 F, s, F-5a'), –181.0 (2 F, s, F-4a', –6a');  $\delta_H$ ( $\text{CDCl}_3$ ) 5.24 (1 H, br s, 5-H), 4.22 and 4.18 (both 1 H, s, 9-H), 2.17, 2.13, and 2.10 (each 3 H, s, 10-, 11- and 12-H<sub>3</sub>).

Table 2. Atomic co-ordinates ( $\times 10^4$ ).

	x	y	z
N(1)	9 009(2)	1 896(1)	4 305(2)
C(11)	8 698(2)	1 446(2)	2 976(3)
C(12)	9 420(2)	891(2)	2 876(4)
C(121)	9 281(3)	299(4)	1 780(5)
C(13)	10 119(2)	1 023(2)	3 778(4)
C(131)	10 988(3)	612(2)	4 006(6)
C(14)	9 993(2)	1 693(2)	4 619(4)
N(2)	8 498(2)	1 719(1)	5 626(3)
C(3)	7 668(2)	1 974(2)	5 517(3)
C(31)	7 154(2)	1 775(2)	6 927(3)
F(31)	6 274(1)	2 012(1)	6 808(2)
C(32)	7 546(3)	2 194(3)	8 273(4)
F(321)	8 368(2)	2 009(2)	8 662(2)
F(322)	7 030(2)	2 086(2)	9 432(2)
F(323)	7 533(2)	2 876(2)	7 999(3)
C(33)	7 100(3)	964(3)	7 193(5)
F(331)	7 005(2)	609(1)	5 948(4)
F(332)	6 419(2)	809(2)	8 034(4)
F(333)	7 846(2)	715(1)	7 851(3)
C(4)	7 368(2)	2 476(2)	4 448(3)
C(41)	6 416(2)	2 586(2)	3 800(3)
F(41)	6 522(1)	2 926(1)	2 441(2)
C(42)	5 744(2)	3 075(1)	4 683(4)
F(421)	6 168(1)	3 433(1)	5 749(2)
F(422)	5 080(1)	2 703(1)	5 299(2)
F(423)	5 341(1)	3 551(1)	3 787(2)
C(43)	5 938(2)	1 894(2)	3 287(4)
F(431)	5 782(1)	1 440(1)	4 358(2)
F(432)	5 157(1)	2 041(1)	2 605(2)
F(433)	6 464(1)	1 554(1)	2 328(2)
C(5)	8 135(2)	2 885(2)	3 956(3)
C(51)	8 132(2)	3 685(2)	3 571(4)
F(51)	7 277(1)	3 964(1)	3 649(2)
C(52)	8 447(3)	3 830(2)	1 981(5)
F(521)	9 335(2)	3 767(2)	1 871(3)
F(522)	8 083(2)	3 383(2)	1 059(2)
F(523)	8 244(2)	4 479(1)	1 566(3)
C(53)	8 688(4)	4 121(2)	4 744(5)
F(531)	9 569(2)	4 006(1)	4 741(3)
F(532)	8 392(2)	3 974(1)	6 056(3)
F(533)	8 564(2)	4 811(1)	4 487(3)
N(6)	8 972(2)	2 662(1)	4 021(2)

**Crystal Data.**— $C_{18}H_{10}N_3F_{21}$ ,  $M = 667.3$ , monoclinic,  $P2_1/n$  (non-standard setting of No. 14),  $a = 14.70(1)$ ,  $b = 18.739(7)$ ,  $c = 9.052(4)$  Å,  $\beta = 91.12(5)^\circ$ ,  $U = 2 492(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.79$  g cm<sup>-3</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.710 69$  Å,  $\mu(\text{Mo-K}\alpha) = 2.09$  cm<sup>-1</sup>,  $F(000) = 1 312$ ,  $T = 298$  K. Final  $R = 0.0507$  for 2 649 observed data.

**Data Collection.**—Graphite monochromated Mo-K $\alpha$  intensity data were collected on a Nicolet P2<sub>1</sub> four-circle diffractometer at 298 K from a light-yellow transparent crystal (approx.

0.5  $\times$  0.4  $\times$  0.4 mm) mounted inside a Lindemann glass capillary under dry nitrogen gas and stuck to the wall with epoxy adhesive. Cell parameters are calculated from 15 centred reflections  $20^\circ < 2\theta < 26^\circ$ . 4 732 Reflection intensities were collected in the bisecting mode by  $\omega/2\theta$  variable speed scans for one quadrant of the reflecting sphere ( $0 \leq 2\theta \leq 50^\circ$ ), for reflection indices in the ranges  $0 < h \leq 18$ ,  $0 < k \leq 23$ ,  $-11 < l \leq 11$ . Two standards (0 -2 1 and -3 -1 0) measured every 100 reflections, and used to scale the data, showed a 3% variation in intensity, but no serious decay during data collection. Of 4 393 'Lp-corrected' unique data, 2 649 were used for structure refinement [ $F > 4\sigma(F)$ ].

**Structure Solution and Refinement.**—The structure was solved by the Direct method procedure 'SOLV' in the SHELXTL suite of programs<sup>10</sup> and refined by blocked cascade least-squares refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically placed (0.96 Å) and allowed to 'ride' on their supporting carbon atom with a fixed isotropic temperature factor of 1.2 times that of the latter.

385 Least-squares parameters were refined to a final  $R$  index of 0.0507,  $R_w = 0.0522$  where  $w = 1/[\sigma^2(F) + gF^2]$  with  $g$  fixed at 0.0003 during the final cycles and  $\sigma(F)$  as the error in  $F_0$  based on counting statistics. Mean and maximum shifts/esd's in the last four cycles of blocked-cascade least-squares refinement were 0.024 and 0.149, respectively. The high thermal parameters of the terminal CF<sub>3</sub> fluorine atoms could suggest rotational disorder in the CF<sub>3</sub> groups. Indeed, the final difference Fourier electron density map showed indications of alternative fluorine sites at C-4b and C-6b with peak heights  $< 0.2$  eÅ<sup>-3</sup>.

Selected interplanar angles for compound (5a) are given in Table 1; selected atomic co-ordinates are given in Table 2. Bond lengths and bond angles, atomic co-ordinates, isotropic thermal parameters, and structure factors have been deposited at the Cambridge Crystallographic Data Centre.

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