

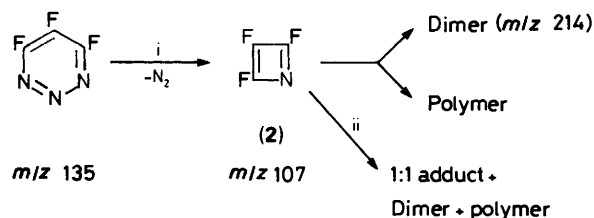
Photochemistry of Halogenocarbon Compounds. Part 6.^{1,2} Direct Observation of Fluorinated Azetes

Richard D. Chambers,* Thomas Shepherd, Masayuki Tamura,† and Peter Hoare
Department of Chemistry, University Science Laboratories, South Road, Durham, DH1 3LE

Low temperature photolyses of trifluoro-1,2,3-triazine and the corresponding perfluoro-4,6-di-isopropyl derivative gave clear evidence of azete formation by observing IR spectra and by transference to a mass spectrometer. Evidence for trapping the preformed azetes, with furan, is presented. Only cleavage of perfluorotri-isopropyl-1,2,3-triazine, to alkyne and nitrile was observed on low temperature photolysis.

Azetes have been observed directly in 'push-pull' systems;³ some benzazete derivatives are relatively stable⁴ and, more recently, remarkably stable tri-*t*-butyl derivatives have been described.⁵ In the preceding paper we discussed generation of fluorinated azetes and described some trapping experiments. Naturally, this has encouraged us to explore direct observation experiments on these rare monocyclic azetes and, indeed, to dispel any doubts about the intermediacy of azetes in the reactions described earlier.¹

Standard low-temperature apparatus was employed (see Experimental section) in which a cooled (liquid-nitrogen) potassium bromide disc was used to condense, under high vacuum, a very thin film of the starting compound. It was then possible to photolyse, through a quartz window, compounds on the disc and then observe the IR spectrum, through potassium bromide windows set at right angles to the quartz. Using this technique a thin film of trifluoro-1,2,3-triazine was photolysed (254 nm) and the IR spectrum was taken at intervals, until it was



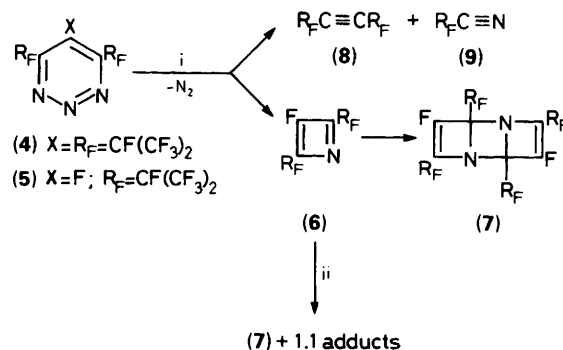
Reagents and conditions: i, hv, 254 nm, 77 K; ii, furan.

clear that further reaction was extremely slow. New absorptions appeared in the C=C and C=N stretching region (Table 1) which are attributable to CF=CF and CF=N of trifluoroazete (2); these stretching vibrations are consistent with values shown for the model compounds indicated in Table 2.⁶ However, further conclusive evidence that (2) existed on the disc at 77 K came from mass spectrometry. Reproducible control experiments were first carried out, in which a film of trifluoro-1,2,3-triazine (1) on the disc at 77 K, was allowed to warm while the apparatus was connected to a mass spectrometer, and the temperature was carefully monitored. It is important to note that the mass-spectrum of (1) contains, as the base peak, m/z 107 ($M^+ - 28$), which also corresponds to M^+ for the azete (2). Analogous observations were carried out with the photolysis product and this also showed the peak at 107, but at *ca.* 15 K lower (*ca.* 213 K) than that for the triazine (1). We took great care to establish that these results were reproducible over

Table 1. Photolysis of fluorinated 1,2,3-triazine derivatives (77 K).

Starting material	IR ($\nu_{\text{max}}/\text{cm}^{-1}$)	m/z	Proposed structure
(1)	{ 1 645 1 675 }	107	Azete (2)
		169 ($M^+ - \text{FCN}$)	Dimer
(4)	2 230 2 160	{ 175 ($M^+ - \text{F}$) 343 ($M^+ - \text{F}$) }	Nitrile (9) Alkyne (8)
(5)	{ 1 650 1 665 1 720 }	407	Azete (6)
		745 ($M^+ - \text{CF}_3$)	Dimer(s) including (7)

several experiments with each system. It is also significant that the spectrum of the triazine (1) does not show m/z 169 (*i.e.* $M^+ - \text{FCN}$ for the azete dimer) and the latter peak appeared for the photolysis product, together with m/z 107. We deduced that the trifluoroazete (2) is very unstable and some dimerisation occurs during the warm up even at 183 K. This is revealed by a lowering of the relative intensities of the 1 645 and 1 675 cm^{-1} bands in the IR spectrum on warming. After reaching ambient temperature and consequent evaporation of volatile material from the plate, a residual polymer remained. An attempt was made to further confirm the production of (2) at low temperatures; a thin film (1) was photolysed and then a film of furan was deposited over the photolysis product at 77 K. On warming, while connected to the mass spectrometer, a new m/z value was observed at 175 which corresponds to M^+ for a 1:1 adduct of (2) with furan. It is worth emphasising, however, that this is a minor product because attempts to trap (2) at ambient temperatures in this way led only to polymer.¹

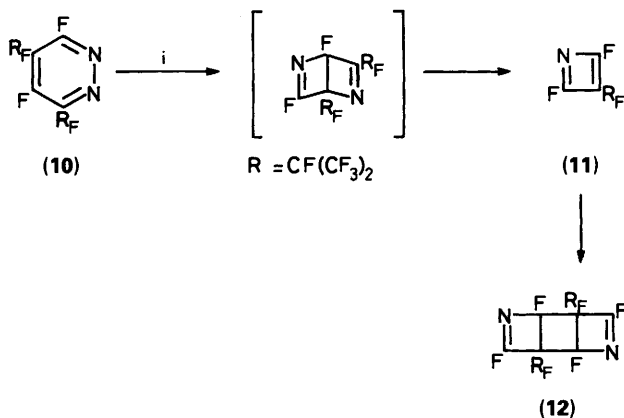


Reagents and conditions: i, hv, 254 nm, 77 K; ii, furan.

† On leave from the Asahi Glass Company Ltd., Japan.

Photolysis of perfluorotri-isopropyltriazine (4) led to fragmentation, even at 77 K, giving the alkyne and nitrile derivatives (8) and (9) respectively. This corresponds with results at ambient temperature and emphatically demonstrates that production of perfluorotri-isopropylazete by this approach is not feasible. In contrast, the perfluorodi-isopropyl derivative (5) gave more efficient conversion to an azete, than (1). Complete conversion of (5) could be observed from the IR spectrum at 77 K, but the new bands above 1350 cm^{-1} (see Table 1) were relatively weak and are not in themselves conclusive. However, on transfer of material to the mass spectrometer, a peak at m/z 407 appeared at a temperature of *ca.* 20 K lower than that at which the corresponding m/z 407 was observed for the starting triazine (5). As the temperature rose, a peak at m/z 745 appeared corresponding to the dimer (7). Further conclusive proof that (6) was generated on the disc was obtained in an experiment where furan was deposited at 77 K, after the photolysis of (5) was completed. On warming to the mass spectrometer, a new peak at m/z 475 was observed, which corresponded to a 1:1 adduct. In this case, however, 1:1 adducts of (6) with furan have been *observed* at ambient temperature but this experiment nicely confirms that these products do, indeed, arise from the azete (6).

It seems clear that trifluoroazete (1) is significantly more reactive than the di-isopropyl derivative (6) and demonstrates again, the stabilising effect of perfluoroalkyl groups on small rings.⁷ Other synthetic approaches to perfluorotri-isopropylazete will be necessary, but it is likely to be much less susceptible to dimerisation than (6). The dimerisation of the azete (6) through $\text{C}=\text{N}^1$ is interesting because it contrasts with the dimerisation of perfluoro-3-isopropylazete (11) which we believe is intermediate in the formation of (12), together with interconvertible isomers, from (10).⁸ The different regiochemistry of dimerisation from (11) and (6) may be due to the maximisation of stabilisation of the four-membered rings by perfluoroalkyl groups at the bridgehead positions for (12).



Conditions: *i*, *hν*, 254 nm, vapour phase, transference conditions.

Since such stabilisation could occur equally for C=C or C=N dimerisation of (6), it appears that C=N dimerisation is preferred. Examples of photochemical $2\pi + 2\pi$ cycloadditions to C=N have been reported for other systems,⁹ although *exo*-isomers are claimed. We, in contrast, have concluded that (7) has the *endo*-structure and the dimerisation (6) \rightarrow (7) may well be best regarded as a $4\pi + 2\pi$ thermal process since, in this paper, we have presented evidence that some dimerisation is occurring *after* photolysis. Additionally, in the previous paper we demonstrated that photolysis of (5) under transference conditions (8 mmHg, N_2), where products were trapped at low temperature, gave (7) when the photolysate warmed up, presumably this occurs by dimerisation of (6) *after* transfer

Table 2. Model compounds, IR absorptions.

X=Bu ^t 1569 ^{5a} X=NMe ₂ 1630 ³	X=Bu ^t 1590 (C=N) ^{5h}
X=Bu ^t 1585 (C=N) ^{5h}	1750 ^{6a} 1735
CF ₃ N=CFCF=NCF ₃	
1650 ^{6b}	1697 ^{6c}
<i>exo</i> 1753 ^{6d} <i>endo</i> 1744	1710 ^{6e} 1630
(Various) 1535 ^{6f} 1620	1650 ¹
1757, 1748 (FC=CF) ^{6g} 1660 (HC=CH)	X=Me 1635 (C=C) 1555 (C=N) X=H 1650 (C=C) 1557 (C=N)
1555 ^{6h}	1605 ¹ 1645 1715
	1600 ¹ 1635 1670 R _f =CF(CF ₃) ₂

Table 3. Photolysis of trifluoro-1,2,3-triazine (1); change in IR spectrum on irradiation at 253.7 nm.

Irradiation (min)	IR absorptions above 1 500 cm ⁻¹ (cm ⁻¹ , intensity †)			
	1 675	1 645	1 635	1 580
(i) 0	—	—	23	77
(ii) 90	15	23	22	70
(iii) 150, 240	27	30	18	69

† Arbitrary units.

and trapping, since dimerisation of (6) under transference conditions is highly unlikely. The same conclusion might also be drawn about the trapping of (2) and (6) with furan.

Experimental

Instrumentation has been described previously.¹⁰

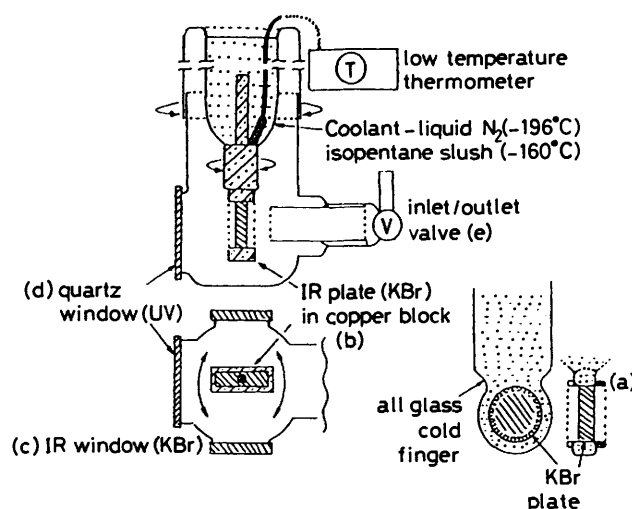
Low Temperature Cell.—The apparatus is a modified version of that used for low temperature IR measurements. It consists of an IR disc (KBr) and holder [(a) aluminium (circular), or (b) copper block] attached to a cryogenic coolant reservoir [(a) is held in loop of the reservoir by a Viton rubber ring, (b) is directly attached to the reservoir by a copper/glass seal]; this assembly is enclosed in a glass jacket having transverse IR windows (KBr) (c), a quartz window (d) perpendicular to the IR plane, and an inlet/outlet trap (e). The cell can be evacuated, and the upper portion including the IR plate holder can be rotated relative to the IR and UV windows, and inlet tap. Before use, the apparatus was evacuated (10⁻² Torr for several hours).

Procedure.—(A) *Deposition and photolysis of sample* (77 K). (i) A sample in the vapour phase (10⁻² Torr), introduced *via* a vacuum line, was deposited on the surface of the KBr disc as a thin film, from tap (e). (ii) Rotation of the disc through 90° was followed by IR measurements of the film. (iii) Further rotation in the same direction (90°) was followed by UV irradiation (253.7 nm). (iv) IR measurement of the photolysed film followed rotation (90°) of the disc in the reverse direction. (v) Finally the photolysate could be transferred to a mass spectrometer *via* inlet (e), after the disc was returned to its original position.

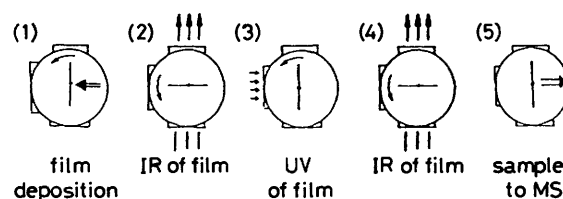
(B) *Mass spectral sampling.* The cell was connected to a mass spectrometer (V.G. Micromass-12) by a minimum length of glass tubing. Volatile materials were transferred from the KBr disc and its temperature rose [evaporation of cryogenic coolant (liquid nitrogen), or replacement of liquid nitrogen by isopentane slush at *ca.* 123 K, followed by controlled warming] towards room temperature. The mass spectrometer, under computer control, recorded the mass spectrum of transferred material at regular intervals (9 s). The approximate temperature was monitored by means of a low-temperature thermocouple placed at the bottom of the coolant reservoir.

(A) *Trifluoro-1,2,3-triazine (1):*¹⁰ *Using the Copper Disc Holder (b).*—(i) *Progress of initial photolysis.*—A very thin film of trifluoro-1,2,3-triazine (1) was deposited on the KBr disc at 77 K. Film thickness was judged by the degree of 'fogging' of the disc (suitable films being almost transparent); also the intensity of the IR absorption of (1) gave a good indication of relative film thickness. Irradiation of the film (253.7 nm, low pressure arcs) proceeded, and the IR spectrum of the film was recorded at regular intervals (Table 3). It was not possible to convert more than *ca.* 50% of the film to product(s), as shown by the persistence of (1) in the IR spectrum, irrespective of film thickness.

(ii) *Mass spectral sampling of material on the KBr disc.* (a) A



Apparatus for low temperature photolysis.



Procedure for low temperature photolysis.

suitable film of (1) was deposited (as above). The coolant (liquid nitrogen) was poured off, and the cell was connected to the mass spectrometer. When the air temperature in the reservoir had reached *ca.* 123 K, isopentane slush (123 K) was added to the reservoir, and recording of mass spectra initiated. The temperatures at which masses at m/z 135 (M^+) and m/z 107 ($M^+ - N_2$) for (1) were first detected are shown in Table 4(a).

(b) A similar film to ii(a) above was irradiated for 2.5 h. Mass spectral sampling was conducted as described. The temperature at which masses m/z 107 [M^+ for azete (2), and $M^+ - N_2$ for starting triazine (1)] and m/z 135 [M^+ for (1)] first appeared are shown in Table 4(b). Also shown is the appearance of m/z 169, due to the dimer of the azete (2) ($M^+ - FCN$).

(c) A suitable film as in ii(a) was irradiated for 2.5 h. A film of furan was deposited over the photolysate at 77 K, and sampling to the mass spectrometer was conducted as described. The appearance of masses at m/z 175 [M^+ for the 1:1 adduct of the azete (2) with furan] is recorded, along with the masses previously mentioned (above), in Table 4(c)

(iii) *Change in the IR spectrum of the photolysis product on warming.* An experiment similar to ii(b) was conducted, but in place of mass spectral sampling, the IR spectrum of the photolysis product was recorded at regular intervals on warming. The results are shown in Table 4(b) for comparison with the results from ii(b).

(B) *Perfluoro-tri-isopropyl-1,2,3-triazine (4):*¹⁰ *Using the Copper Disc Holder (b).*—A film of perfluoro-tri-isopropyl-1,2,3-triazine (4), on irradiation (253.7 nm) at 77 K for 2 h, gave a product consistent with a mixture of perfluoroisobutyronitrile (9) and perfluoro-2,5-dimethylhex-3-yne (8). This was confirmed when the photolysate was transferred to the mass spectrometer, with masses observed at m/z 175 ($M^+ - F$) for (9) and m/z 343 ($M^+ - F$) for (8). The results are shown in Table 1.

(C) *Perfluorodi-isopropyl-1,2,3-triazine (5):*¹⁰ *Using the Aluminium Disc Holder (a).*—(i) *Progress of initial photolysis.*

Table 4. Mass spectral sampling of photolysis product(s) from (1): direct observation of the azete (2), and trapping of (2) with furan.

Conditions	Temp. (K)	Mass observed (m/z)	Assignment	Change in IR spectrum
(a)	{ 228 and above 238 and above	107 135	(1) $M^+ - N_2^*$ (1) M^{+*}	Broadening and reduction of intensity of absorption at 1 675 and 1 645 cm^{-1}
(b) Irradiation for 2.5 h	{ 183–213 213 and above 231 and above 298	{ 107 169† 135	(2) M^+ dimer of (2) – FCN† Residual triazine (1) Polymer	
(c) Irradiation for 2.5 h, furan added	{ 225 and above 235 241 and above 248 and above 261	169 175 107 135 175	Dimer of (2) – FCN 1:1 adduct, M^+ (2)/furan Unchanged (1) $M^+ - N_2$, M^+ respectively 1:1 adduct, M^+ (2)/furan	

* The same result was obtained for thicker films of (1). † It is not possible to tell whether FCN is lost from the dimer of (2) on the KBr disc, or in the mass spectrometer. Pentafluoropyridine (M^+ , m/z 169), the product of loss of FCN from the dimer, was detected under the same conditions at 193 K, 30 K lower than the observed mass.

Table 5. Photolysis of perfluoroisopropyl-1,2,3-triazine (5), change in IR spectrum on irradiation at 253.7 nm.

	Irradiation (min)	IR absorptions above 1 350 cm^{-1} (cm^{-1} , intensity*)				
		1 720	1 665	1 605	1 535	1 400
(i)	0	—	—	—	21	23
(ii)	15	3	1	6	16	18
(iii)	30	6	5	8	8	9
(iv)	45	7	8	10	6	7
(v)	60	5	9	9	—	—
(vi)	90, 120	5	12	9	—	—

* Arbitrary units.

Table 6. Mass spectral sampling of the photolysis product(s) of (5); direct observation of the azete (6) and trapping of (6) with furan.

Conditions	Temp. (K)	Mass observed (m/z)	Assignment
(a)	{ 263 and above 268 and above	407 435	(5) $M^+ - N_2$ (5) M^+
(b) Irradiation for 1 h*	{ 243–248 258–268 268 and above	407 745 435/407	(6) M^+ (7) $M^+ - CF_3$ (5) (residual)
(c) Irradiation for 1 h, furan added	{ 263–273 278	475	1:1 adduct M^+ , † [furan/(6)]

* No change in IR spectrum of photolysate, material desorbs 263–273 K. † A 1:1 adduct also detected (GC-MS) in residue on plate after warming to room temperature.

A thin film of perfluoro-di-isopropyl-1,2,3-triazine (5) was deposited on the KBr disc at 77 K. Irradiation (253.7 nm) was started and progress was monitored by means of IR spectroscopy (Table 5). It was found that complete photolysis of the triazine (5) to the photolysis product was achieved after *ca.* 1 h.

(ii) *Mass spectral sampling of material on the KBr disc.* (a) A thin film of (5) was deposited at 77 K and then the cell was connected to the mass spectrometer. The coolant (liquid

nitrogen) was allowed to boil off, and recording of mass spectra initiated. The temperatures at which m/z 435 (M^+) and m/z 407 ($M^+ - N_2$) for (5) were first observed are shown in Table 6(a).

(b) A film of (5) was irradiated for 1 h and then mass spectral sampling was conducted as above in ii(a). The appearance of masses at m/z 407 [M^+ for the azete (6) and $M^+ - N_2$ for the triazine (5)], m/z 435 [M^+ for (5)] and m/z 745 [$M^+ - CF_3$ for the dimer(s) of (6)] were recorded, and are shown in Table 6(b).

(c) The above procedure was followed, with a film of furan deposited over the photolysate on completion of irradiation, before sampling with the mass spectrometer. New masses observed were at m/z 475 (M^+) for the 1:1 adduct of (5) with furan. In addition, background masses corresponding to the dimer of (5) were also observed [Table 6(c)].

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