Azetes from Fluorinated 1,2,3-Triazines

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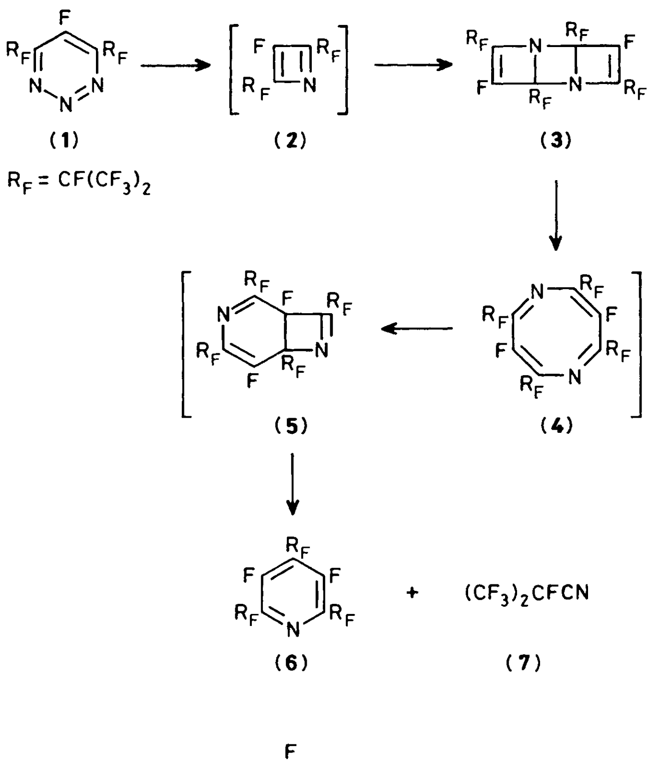
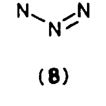
Strong evidence is presented for generation of azetes by photolysis of fluorinated 1,2,3-triazine derivatives; a monocyclic azete has been trapped chemically and another has been observed at low temperature by i.r. and mass spectroscopy.

There is considerable interest in the possible generation of azetes[1—7] but the only derivatives actually isolated are tris(dimethylamino)azete,[1] benzazete derivatives,[2] and, more recently, tri-t-butylazete.[3] In previous work from this laboratory we attempted to generate azete derivatives from halogenated-pyridazine and -1,2,4-triazine derivatives and dimers of a corresponding azete were obtained by photolysis of perfluoro-3,5-di-isopropylpyridazine.[4] Also, rearrangement of an intermediate is most likely in the formation of trichloroacrylonitrile from trichloro-1,2,4-triazine.[5] Here, we report unambiguous evidence for the generation, trapping, and direct observation of azetes derived from fluorinated 1,2,3-triazine derivatives.

The accompanying communication describes the synthesis of fluorinated 1,2,3-triazines.[9] Photolysis of the triazine (**1**) led to quantitative formation of a dimer (**3**) of the corresponding azete (**2**). The structure of (**3**) was established from a variety of data, *e.g.* an i.r. absorption at 1650 cm^{-1} (C=C) and the presence of resonances arising from four tertiary fluorine atoms in the ^{19}F n.m.r. spectrum of (**3**) at δ 185.5 and 185.8 p.p.m. (each rel. int. 2) and two fluorine atoms at vinylic positions [δ 112.4 (d, *J* 56.2 Hz, 1F) and 113.0 p.p.m. (d, *J* 56.2 Hz, 1F)]. It appears that these vinylic positions are rendered slightly non-equivalent by the rotational preferences of the bulky perfluoroisopropyl groups. Any alternative dimerisation through formation of N–N bonds, while being unlikely, is also ruled out by pyrolysis of (**3**) at 350 °C, which resulted in quantitative formation of the known perfluoro-2,4,6-tri-isopropylpyridine (**6**),[10] together with nitrile (**7**). The process most probably involves the intermediate 1,5-diazocine (**4**) and the bicyclic isomer (**5**) because the result is similar to the reported conversion of hexaphenyl-1,5-diazocine into pentaphenylpyridine and benzonitrile.[6] Evidence for the *endo*-structure of (**3**) will be presented in later publications.




(**8**)


(**9**)

In order to observe azetes directly, photolyses (254 nm) of (**1**) and of trifluoro-1,2,3-triazine (**8**) were carried out at 77 K on a KBr disc, without matrix material. I.r. spectra of the photolysates were recorded at 77 K and then mass spectra were obtained, at different temperatures as the system warmed to room temperature, by connecting the apparatus directly to the mass spectrometer. Results are in Table 1.

Photolysis of trifluoro-1,2,3-triazine (**8**) at room temperature gave a polymer but at 77 K, two absorptions near 1650 cm^{-1} (Table 1) can be assigned to C=C and C=N in the azete (**9**), by comparison with appropriate model systems. Furthermore, on warming to −58 °C the mass spectrum showed a parent peak at *m/z* 107, which corresponds to C_3F_3N, while the spectrum of (**8**) was absent. As the temperature of the system was raised, a peak at 169 (C_5F_5N) increased, possibly arising from loss of FCN from a dimer of (**9**). Interestingly, the i.r. spectrum of the photolysate of (**1**) showed only weak absorptions above 1350 cm^{-1} even though, on warming, the mass spectrum showed a parent peak at *m/z* 407 (at −40 °C) and then a peak at *m/z* 745 as the temperature was raised. This clearly indicates the formation of (**2**) at low temperature, which dimerises as the temperature is raised. That (**2**) was present on the KBr disc at low temperature was confirmed by condensing furan onto the disc at low temperature. Warming then led only to a mass spectrum corresponding to a 1 : 1 adduct of (**2**) and furan. Thus, the formation of (**2**) and (**9**) are

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

Starting material	I.r.[a] $\nu_{max.}$/cm^{-1}	*m/z*	Proposed structure
(**1**)	1605 (w)	407	Azete (**2**)
	1665 (w) 1720 (w)	745 (M^+ −CF_3)	Dimers
(**8**)	1645 1675	107	Azete (**9**)
	1720 (vw) 1760 (vw)	169	C_5F_5N

[a] New absorptions above 1350 cm^{-1}.

clearly established and their transference to a mass spectrometer occurs at −40 °C. The fact that only weak i.r. absorptions at wavelengths >1350 cm^{-1} could be detected for (**2**) is most likely due to weak absorption for the $R_FC=CF$ [which is true for dimer (**3**)] and $R_FC=N$ units, but the possibility that (**2**) is partly in the form of an azatetrahedrane, which would not absorb, cannot be entirely ruled out. Theoretical studies, however, indicate no energy minima for azatetrahedrane.[11]

Formation of dimer (**3**) represents a rare example of cycloaddition involving a C=N system[12] and we have also demonstrated that (**2**) can be trapped with furan by photolysis of (**1**) in the presence of excess of furan at room temperature, to give three 1:1 cycloaddition products. The structures of these compounds will be discussed fully in subsequent publications but these experiments represent the first trapping of a monocyclic azete.

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References

1 G. Seybold, U. Jersek, and R. Gompper, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 847.

2 B. M. Adger, C. W. Rees, and R. C. Storr, *J. Chem. Soc., Perkin Trans. 1*, 1975, 45.

3 U. J. Vogelbacher, M. Regitz, and R. Mynott, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 842.

4 R. D. Chambers and J. R. Maslakiewicz, *J. Chem. Soc., Chem. Commun.*, 1976, 1005.

5 R. D. Chambers, W. K. R. Musgrave, and D. E. Wood, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1978.

6 E. M. Burgess and J. P. Sanchez, *J. Org. Chem.*, 1973, **38**, 176.

7 G. Maier and U. Schafer, *Liebigs Ann. Chem.*, 1980, 798.

8 P. Eisenbarth and M. Regitz, *Chem. Ber.*, 1984, **117**, 445.

9 R. D. Chambers, M. Tamura, J. A. K. Howard, and O. Johnson, preceding communication.

10 R. D. Chambers, R. P. Corbally, and W. K. R. Musgrave, *J. Chem. Soc., Chem. Commun.*, 1969, 127.

11 R. M. Minaev and V. I. Minkin, *Teoreticheskaya i Eksperimental'naya Khimiya, Engl. Transl.*, 1980, **16**, 471.

12 (a) S. F. Forgues and N. Paillous, *J. Org. Chem.*, 1986, **51**, 672; (b) D. Lawrenz, S. Mohr, and B. Wendlander, *J. Chem. Soc., Chem. Commun.*, 1984, 863, and references contained.