

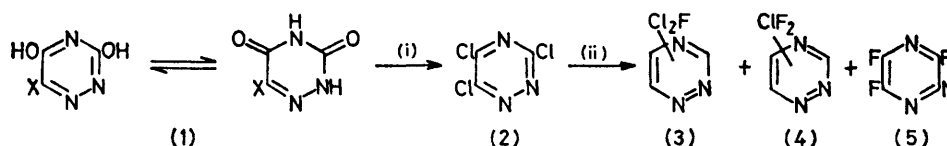
Polyhalogenoaromatic Compounds. Part 30.¹ Eliminations of Molecular Nitrogen from Trichloro- and Perfluorotri-isopropyl-1,2,4-triazine

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Fluorination of trichloro-1,2,4-triazine (2), using potassium fluoride at elevated temperatures is not a useful route to the corresponding trifluoro-derivative but reaction of (2) with hexafluoropropene and potassium fluoride gave perfluorotri-isopropyl-1,2,4-triazine (8). Pyrolysis of (2) in the vapour phase gave trichloroacrylonitrile and this is interpreted as evidence for an intermediate azete. Pyrolysis of (8) gave a mixture of $(CF_3)_2CFC\equiv CCF(CF_3)_2$ (16) and $(CF_3)_2CFCN$ (17) while photolysis gave rearrangement to perfluorotri-isopropyl-1,3,5-triazine (18) as well as (16) and (17) by elimination of nitrogen.

In previous parts of this series, we have been exploring the generality of the synthesis of highly fluorinated nitrogen heterocyclic compounds by nucleophilic displacement of chlorine from their perchlorinated precursors, using potassium fluoride and usually in the absence of a solvent. Here we investigate the 1,2,4-triazine system.

Synthesis of trichloro-1,2,4-triazine (2) is not straightforward. The chlorinations of 3,5-dihydroxy-1,2,4-triazine (1; X = H) and the corresponding 6-bromo-derivative (1; X = Br) have been investigated by several workers,²⁻⁴ using phosphoryl chloride and/or phosphorus pentachloride and, in some cases, base catalysis was employed. Loving and his co-workers⁴ claimed high yields of trichloro-1,2,4-triazine (2) starting



Reagents: (i) PCl_5 , Ni autoclave, 200 °C, 2 h; (ii) KF, autoclave, < 200 °C

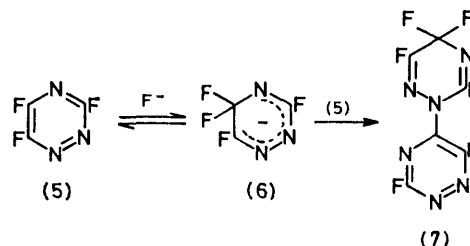
with (1; X = Br) but, in our hands, the procedures described gave low yields of (2). Higher yields (36–48%) of (2) were obtained, however, by using phosphorus pentachloride and (1; X = Br) without a solvent in an autoclave; this is a method that we have used previously for chlorination of a series of azines and diazines.⁵ Using the same procedure with 3,5-dihydroxy-1,2,4-triazine (1; X = H) gave only low yields (19–33%) of (2).

In principle, conversion of trichloro-1,2,4-triazine (2) to the corresponding trifluoro-derivative, using potassium fluoride, should be a very easy process because it is well known that both trichloro-1,3,5-triazine⁶ and tetrachloropyridazine⁷ are converted into their perfluoro-analogues using this procedure. Surprisingly, however, comparable reactions of (2) are much more complicated. Reaction of (2) with potassium fluoride in an autoclave at various temperatures below 200 °C gave mixtures of products (ca. 34–58% yield) containing isomeric dichloro- and chlorodifluoro-1,2,4-triazines (3) and (4), respectively, and only a trace of trifluorotriazine (5). Above 200 °C only low yields of compounds corresponding in molecular weight to dimers of (5) were isolated. The formation of dimers, e.g. (7), could occur through

reaction of a σ -complex (6) with trifluorotriazine (5), since σ -complexes formed between trifluoro-1,3,5-triazine and caesium fluoride have been identified.⁸ Also, fluoride-ion-induced ring-opening, leading to high molecular weight material, is probably another complicating feature at higher temperatures. Indeed, when (2) was mixed with caesium fluoride at room temperature, a vigorous reaction took place, leaving an intractable solid. This is similar to the observation that a clear glass of unknown structure is formed by heating an equimolar mixture of caesium fluoride and trifluoro-1,3,5-triazine.⁸

Introduction of perfluoroisopropyl groups into (2) was achieved smoothly, however, using hexafluoropropene and potassium fluoride in a solvent. Even though only

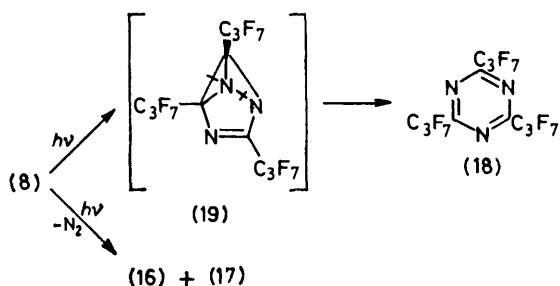
traces of the fluorinated derivatives (3)–(5) are isolated from this system in the absence of hexafluoropropene, it is probable that chlorine is replaced by fluorine, giving (3)–(5), prior to polyfluoroalkylation which would then activate the system towards polyfluoroalkylation. This



conclusion is substantiated by the fact that in analogous experiments, but using amounts of potassium fluoride that were insufficient for both halogen exchange and catalysis, neither polyfluoroalkylation nor oligomerisation⁹ of the hexafluoropropene occurred, thus indicating that the fluoride is used in the prior halogen exchange. Small amounts of a mixture of two perfluorodi-isopropyl-1,2,4-triazines were detected by mass-spectrometry-g.l.c.

flow system at *ca.* 600 °C giving approximately equimolar mixtures of (16) and (17). If a diradical intermediate is produced from (8), which is the analogue of (14c), then migration of perfluoroisopropyl is clearly less preferable to further fragmentation to (16) and (17).

Photolysis of (8) occurs when the system is sensitised by benzophenone, and products (16) and (17) (total yield 11.3%) arising from loss of nitrogen were observed together with the product of rearrangement, *i.e.* perfluorotri-isopropyl-1,3,5-triazine (18). Although other processes could be written, the most simple explanation for the formation of (18) involves formation of the triaza-benzvalene derivative (19) as an intermediate, in a process



which is analogous to that advanced to account for the highly specific thermal rearrangement of some perfluoroalkylpyridazines.¹²

EXPERIMENTAL

Spectroscopic data were obtained with the following spectrometers: *i.r.*, Grubb-Parsons Spectromaster; *u.v.*, Perkin-Elmer 547 or 577; mass, A.E.I. MS9 or V.G. Micromass 12B linked with *g.l.c.*; *n.m.r.*, Varian A56/60D. Where indicated by an asterisk, full spectroscopic data are available in Supplementary Publication No. SUP 22467.*

6-Bromo-3,5-dihydroxy-1,2,4-triazine (1; X = Br).—A solution of glyoxylic acid semicarbazone² (31 g, 0.242 mol) in ethylene glycol (1 l) was added rapidly to sodium (18 g, 0.78 mol) dissolved in absolute ethanol (0.5 l) and the solution was heated under reflux for 24 h. Solvent was removed under vacuum at 120 °C, the residue was dissolved in hot water (0.5 l), and the hot solution was adjusted to pH 2 with concentrated hydrochloric acid. 3,5,6-Trihydroxy-1,2,4-triazine (1; X = OH) crystallised on cooling and was recrystallised from water (18.7 g, 68%), *m.p.* 266–269° (*lit.*,² 268–270°). A mixture of this material (18 g, 0.16 mol), bromine (18 g, 0.228 mol), and water (270 ml) was stirred for 27 h. The crystalline material was filtered off, recrystallised from water, and dried under vacuum to yield the bromotriazine (1; X = Br) (16.7 g, 54%), *m.p.* 239–241° (*lit.*,¹⁶ 232–234°).

3,5,6-Trichloro-1,2,4-triazine* (2).—A mixture of (1; X = Br) (34.5 g, 0.179 mol) and phosphorus pentachloride (150 g) was sealed in a nickel-lined autoclave which was placed in a furnace at 200 °C and maintained at this temperature for 2 h. On cooling, the product was removed from the autoclave and POCl₃ (formed in the reaction) was removed under reduced pressure. Distillation at 50–70° and 0.05 mmHg, followed by recrystallisation from hexane

gave 16.2 g (49%) of product. Further purification by vacuum sublimation gave the pure triazine (2) [Found: C, 19.8; Cl, 57.9; N, 22.4%; *M*⁺, 183 (³⁵Cl). Calc. for C₃Cl₃N₃: C, 19.5; Cl, 57.7; N, 22.8%; *M*, 183], *m.p.* 57–59° (*lit.*,⁴ 60–62°).

Attempted Fluorinations of (2).—Reactions were carried out at a variety of temperatures using carefully dried potassium fluoride and an autoclave which had been dried in an oven. Mixtures of (2) with potassium fluoride were made up and transferred to the nickel-lined autoclave, all procedures being carried out under dry nitrogen in a glove-bag. Volatile products were removed under vacuum from the hot autoclaves and, from reactions carried out at temperatures below 200 °C, the products, when analysed by *m.s.-g.l.c.*, contained *M*⁺ 167 (C₃Cl₂FN₃), *M*⁺ 151 (C₃ClF₂N₃), and a minor component, *M*⁺ 135 (C₃F₃N₃). However, the quantities of these materials were insufficient for separation. In reactions using temperatures >200 °C, only small amounts of volatile material, giving *M*⁺ 270 (C₆F₆N₆) were obtained. Only intractable materials were isolated by extraction with chloroform of the residues in the autoclave.

Perfluoro-3,5,6-tri-isopropyl-1,2,4-triazine* (8).—The technique employed is one which has been used for introduction of perfluoroalkyl groups into other aromatic systems.¹⁷ A mixture of anhydrous potassium fluoride (5.03 g, 0.087 mol), sulpholan (20 ml), and 3,5,6-trichloro-1,2,4-triazine (4.0 g, 0.022 mol) was stirred in a flask fitted with a gas-tap and a variable volume reservoir. The apparatus was evacuated and then filled with hexafluoropropene (9.78 g, 0.065 mol); the resulting system was stirred at room temperature for 24 h, by which time all of the gas had been used up. Volatile material was then transferred out of the reaction mixture under vacuum, and the main component was separated by fractional distillation at atmospheric pressure, to give (8) as a yellow liquid (7.9 g, 61%), *b.p.* 155° (Found: C, 24.9; F, 68.6; N, 7.6%; *M*⁺, 585. C₁₂F₂₁N₃ requires C, 24.6; F, 68.2; N, 7.2%; *M*, 585). In the fractional distillation, a preliminary fraction was obtained which contained two components. These could not be separated but mass spectrometry-*g.l.c.* showed these to be isomeric perfluorodi-isopropyl-1,2,4-triazines (*M*⁺ 435).

Pyrolysis of 3,5,6-Trichloro-1,2,4-triazine (2).—Dry nitrogen was passed through molten 3,5,6-trichloro-1,2,4-triazine (5.4 g, 0.029 mol) at 100 °C. The nitrogen stream was then passed through a silica tube lined and packed with platinum foil at 660 °C, at a rate estimated to give a contact time of *ca.* 12 s. The product was collected in a cold trap and was identified as trichloroacrylonitrile* (2.06 g, 45%) by comparison of spectra (including ¹³C *n.m.r.*). An authentic sample of trichloroacrylonitrile was prepared for comparison.¹⁸

A sample of (2) (1.1 g, 6.0 mmol) was heated at 300° in an evacuated Carius tube for 6 days. After cooling, the tube was opened and trichloroacrylonitrile (0.07 g) was transferred under vacuum.

Pyrolysis of Perfluoro-3,5,6-tri-isopropyl-1,2,4-triazine (8).—A sample of (8) (1.89 g) contained in a carefully dried nickel tube sealed under nitrogen was heated at 450 °C for 40 min. On cooling, volatile material (1.70 g) was removed under vacuum. Analysis of the product by ¹⁹F *n.m.r.* and *m.s.-g.l.c.* showed an equimolar mixture of perfluoro-2,5-dimethylhex-3-yne* (16) (*M*⁺, 362), δ_F 80 (6 F, d, *J* 10 Hz) and 175 (1 F, heptet) *p.p.m.*, and perfluoroisobutyronitrile* (17).¹⁹

* See Notice to Authors No. 7 in *J.C.S. Perkin I*, 1978, Index issue.

In a flow system, samples of (8), carried in a stream of dry nitrogen, were passed through a platinum-lined silica tube (contact time *ca.* 12 s) at various temperatures. Below 500 °C little reaction occurred but in a reaction using (8) (1.1 g) at a tube temperature of 600 °C the volatile products (0.95 g) were identified as an equimolar mixture of (16) and (17).

Photolysis of (8).—An evacuated silica Carius tube containing compound (8) (1.0 g, 1.7 mmol), benzophenone (3.8 mg), and CF₂ClCF₂Cl (*ca.* 30 ml) was irradiated with a low pressure mercury lamp (120 W) for 129 h. Contents were recovered from the tube by vacuum transfer and the bulk of solvent was removed by careful fractional distillation. Analysis of the remaining material by m.s.–g.l.c. showed (8) (83%), (16) and (17) (11.3%), and perfluoro-2,4,6-tri-isopropyl-1,3,5-triazine (18) (5.7%); an authentic sample of (18) was synthesised²⁰ for comparison of spectra.

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