# Heterocyclic Polyfluoro-compounds. Part 39.[1] Preparation and some Nucleophilic Substitution Reactions of Trifluoro-1,2,4-triazine

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Fluorination of trichloro-1,2,4-triazine over potassium fluoride at 450 °C in a flow system yields trifluoro-(91%) and 6-chloro-3,5-difluoro-1,2,4-triazine (5%). The trifluorotriazine yields a dimer with time, which reverts to the monomer with potassium fluoride at 250 °C, and gives 6-fluoro-1,2,4-triazine-3,5(2H,4H)-dione (45%) with water, 5-amino-3,6-difluoro-1,2,4-triazine (76%) with ammonia, a 3,5-bis(4-chloroanilino)-derivative (50%) with p-chloroaniline, 3,5-bis(diethylamino)-6-fluoro-1,2,4-triazine (45%) with diethylamine, and a 1:2 mixture of 3,5- and 5,6-dimethoxy-derivatives (41%) with methanol.

FLUORINATION with potassium fluoride in the absence of solvent of chlorinated heterocycles is usually the preferred method for preparing highly fluorinated heterocycles. Pentachloropyridine,[2] tetrachloro-pyrimidine,[3] -pyridazine,[4] and -pyrazine,[5] and trichloro-1,3,5-triazine[6] are readily converted into their respective perfluorinated analogues by this method. We here describe the preparation of trifluoro-1,2,4-triazine, and some of its nucleophilic substitution reactions.

The fluorination of trichloro-1,2,4-triazine[7] with potassium fluoride proved unexpectedly difficult. Small-scale experiments in sealed Pyrex ampoules indicated that a temperature of 225 °C for 72 h was optimal, but the reaction proved to be very erratic and difficult to reproduce on a larger scale. Fluorinations in aprotic solvents proved equally temperamental and, eventually, a flow method was devised which obviated all these problems. Passage of the vapour of trichloro-1,2,4-triazine over a cylindrical bed of potassium fluoride, which had a small space along the axis to aid transport of the reactant and products and was heated to 450 °C, gave excellent yields (>90%) of trifluoro-1,2,4-triazine (1), along with small amounts of 6-chloro-3,5-difluoro-1,2,4-triazine (2), and a dimer of the trifluorotriazine.
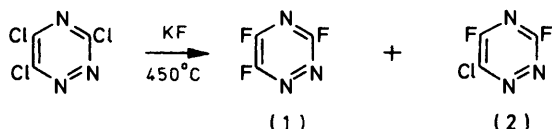

A trace of the symmetrical trifluoro-1,3,5-triazine appeared to be present by i.r. spectroscopy.

Trifluoro-1,2,4-triazine, a very moisture-sensitive liquid, dimerised with time, and this was accelerated by traces of water or fluoride ion. The dimer was assigned structure (3) for the following reasons.

In its ^{19}F n.m.r. spectrum, it showed two absorptions indicative of 3,6-fluorines in a 1,2,4-triazine ring (see below), with shifts similar to those of the ring fluorines in perfluoro-(5-dimethylamino-1,2,4-triazine).[8] The other ring showed two absorptions with an 18 Hz coupling indicative of 1,4-fluorines in a 1,3-diene fragment.[9] A 24 Hz coupling of the CF_2 fluorines to one of these indicated a three-bond coupling, and an inter-

ring coupling of 18 Hz involving the other olefinic fluorine, somewhat larger than the analogous inter-ring coupling constant in perfluoro-(4-phenylpyrimidine),[10] and may well have a ' through-space ' contribution, when the conformation shown is the favoured one. The dimer, when passed over potassium fluoride at 250 °C, reverted to the monomer, so that the formation of (3) is reversible.

(3)
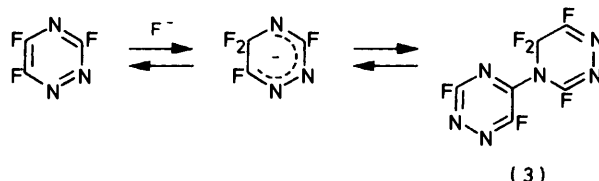
So far as nucleophilic substitution in trifluoro-1,2,4-triazine is concerned, the expected order of reactivity is F-5 > F-3 > F-6. In azines where substitution occurs by the S_NAr mechanism, those intermediate σ-complexes are favoured where the negative charge resides on a ring nitrogen, with para-quinonoid forms favoured more than ortho-quinonoid.[11] If these σ-complexes are good models for the transition states, the above order follows. A recent study of aromatic nucleophilic substitutions by Chambers and his co-workers has emphasised the importance of fluorine substituents ortho and meta to the site of attack in stabilising the intermediate σ-complexes,[12] and this emphasises the above order.

This expectation was largely borne out in practice. Trifluoro-1,2,4-triazine fumed in moist air, and 6-fluoro-1,2,4-triazine 3,5(2H,4H)-dione (4) (45%) was formed
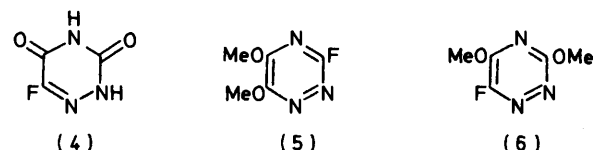
with water. The dione structure follows from its i.r. spectrum, where like other 5-substituted azauracils,[13] it shows strong C=O stretching at 1 690 and N–H stretching around 3 150 cm^{-1}. Like the 6-chloro- (m.p.,[14] 232—233 °C) and 6-bromo-analogues (m.p.,[7] 232—234 °C), it has a high melting point (m.p. 226—229 °C).

With methanol, a 2 : 1 mixture of two dimethoxy-derivatives (5) and (6) was obtained. The 5,6-dimethoxy-derivative was unexpected, and the structure rests upon [19]F n.m.r. evidence. The [19]F n.m.r. spectrum of the mixture showed two singlets at 9.8 and −30.0 p.p.m. (positive values to low-field of external trifluoroacetic acid). Trifluorotriazine has absorptions at 15.9 (F-3), 4.6 (F-5), and −24.9 p.p.m. (F-6) with $|^3J| = 23$, $|^5J| = 34$ Hz, and $|^4J|$ not resolved. The assignment follows by analogy with other azines, *ortho*-nitrogen atoms causing a low-field shift, and the coupling constant magnitudes are in accord with those of fluoropyridines [15] and pyrimidines.[3] If the substituent shifts for methoxy in fluoropyrimidines [3] are used to predict shifts in dimethoxyfluoro-1,2,4-triazines, they predict that the 3,5-isomer should absorb at −36.3, the 5,6-isomer at 5.1, and the 3,6-isomer at 0.7 p.p.m., whence the assignment of the 3,5-isomer seems sure, while that of the 5,6-isomer is only slightly less certain. A mixture of 3,5- and 5,6-dimethoxy-derivatives is also obtained when trichloro-1,2,4-triazine is treated with two equivalents of sodium methoxide.[14]

Ammonia displaces only the 5-fluorine, and the magnitude of $|^5J|$ displayed (36 Hz) supports this assignment. In the proton n.m.r. spectrum (in [$^2H_6$]acetone), a broad singlet appears at δ 7.9 p.p.m., and the i.r. spectrum shows a band at 1 668 cm⁻¹, absent from trifluoro-1,2,4-triazine, and a series of bands around 3 000 cm⁻¹, resembling somewhat those of compound (4). Structure (7) is therefore favoured, this particular

(7)   (8)
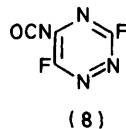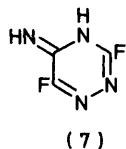
tautomer being indicated by the large value of the coupling constant. The shift to shorter wavelengths in the u.v. spectrum, compared with that of trifluoro-1,2,4-triazine, supports this.

With 4-chloroaniline, the expected 3,5-disubstituted derivative was obtained, and the [1]H n.m.r. spectrum of this indicated two quite distinct types of *p*-disubstituted benzene ring, so that again an imino-structure is favoured. This was supported by the i.r. spectrum. With diethylamine also, a 3,5-disubstituted derivative resulted, but here, where no imino-form is possible, there were no bands in the 1 600—1 700 cm⁻¹ region.

The trifluoro-1,2,4-triazine showed considerable resistance to both pyrolysis and photolysis in the vapour phase. When subjected to flow pyrolysis at 800 °C in silica, it underwent a small amount of fragmentation, was largely recovered (82%), formed a trace of cyanuric fluoride, and gave small amounts of a compound tentatively identified (mass and i.r. spectra) as the 5-isocyanatotriazine (8). Pentafluoroazapropene reacts with silica to give trifluoromethyl isocyanate.[16] Fragmentation of the dimer (3) with loss of 2FCN would give an

N=CF_2 substituted triazine, which could then react with silica to give compound (8).

Very recently, unsuccessful attempts to synthesise trifluoro-1,2,4-triazine by fluorination of the trichloro-compound with potassium fluoride in autoclaves were described.[17] In the light of our initial difficulties this failure is understandable, but the flow fluorination, which may have advantages with other very reactive substrates, makes trifluoro-1,2,4-triazine readily available.

EXPERIMENTAL

Volatile materials were manipulated in a Pyrex vacuum system. Products were identified by elemental analysis, i.r. spectroscopy (Perkin-Elmer models 257 or 397), u.v. spectroscopy (Cary 118x spectrophotometer), n.m.r. spectroscopy [Perkin-Elmer R32 operating at 90 MHz for protons (tetramethylsilane reference) and 84.6 MHz for [19]F (external trifluoroacetic acid reference), where positive values of chemical shifts are to low field of the reference], mass spectrometry (Kratos MS45 at 70 eV), and g.l.c. (Pye 104 or Pye-Unicam model GCD instruments).

Molecular weights were obtained by mass spectrometry.

Preparation of Trichloro-1,2,4-triazine.[7]—To 6-bromo-1,2,4-triazine-3,5($2H,4H$)-dione [18] (4.8 g, 25 mmol) in phosphorus oxychloride (100 cm³) was added phosphorus pentachloride (10.4 g, 5 mmol) and NN-diethylaniline (10 cm³, 75 mmol). The mixture was stirred and heated under reflux for 2 h, after which it was set aside at room temperature for 24 h; the excess of solvent was then removed under reduced pressure and the residue was continuously extracted with diethyl ether. Removal of the diethyl ether from the extract left a thick brown oil, which was sublimed three times at 60 °C *in vacuo* to give trichloro-1,2,4-triazine (2.1 g, 11.3 mmol, 45%), m.p. 56—58 °C (lit.,[7] 57—58 °C). The triazine was stored in a dark bottle under nitrogen.

Yields up to 50% were obtained routinely on this scale, but when attempts were made to scale up the reaction ten times, they fell considerably, apparently because it was difficult to sublime or distil the moisture-sensitive product from the tar obtained by ether extraction.

Preparation of Trifluoro-1,2,4-triazine.—Experiments in which trichloro-1,2,4-triazine was heated with an excess of anhydrous potassium fluoride in a sealed Pyrex ampoule gave yields of ca. 30% of trifluoro-1,2,4-triazine, when carried out on a 1-g scale at 225 °C for 72 h, but the material was contaminated with 6-chloro-3,5-difluoro-1,2,4-triazine, and sometimes dichlorofluoro-1,2,4-triazines, and the dimer (see below). Further, the experiment was very sensitive to temperature variations, gave erratic yields, and was not scaled up satisfactorily.

Reactions were also attempted using potassium fluoride in 1-methyl-2-pyrrolidine (unsuccessful), sulpholane at 170 °C for 0.5 h, where 42% of the trifluoro- and 35% of the chlorodifluoro-triazines were obtained, and tetraglyme at temperatures up to 200 °C for 0.5 h, where yields of up to 95% of mixed triazines could be obtained; the reactions proved very erratic, however, and frequently gave negligible yields. Eventually the following flow method was adopted. Powdered potassium fluoride (ca. 120 g, 2.07 mmol), which had been dried at 70 °C, was poured into a Pyrex tube (24 mm i.d. × ca. 350 mm) which had a central glass rod (4 mm

diam.). The tube was placed in a horizontal furnace, and the glass rod was then carefully removed, leaving an axial hole in the bed of potassium fluoride, which was contained between glass wool plugs. The tube, which was fitted with a wide-bore tap at one end and had a cold trap attached at the other end, was carefully evacuated and then the potassium fluoride dried at 450 °C overnight. A small flask containing trichloro-1,2,4-triazine (10.0 g, 54 mmol) was then attached to the tap, evacuated, and heated to 60 °C along with the tap with heating tape. The triazine sublimed at 0.2 mmHg through the tube at 450 °C over a period of *ca.* 4 h (estimated contact time *ca.* 0.5 s based on the volume of the tube not occupied by KF) and the product was collected in the trap cooled to −196 °C. Trap-to-trap distillation *in vacuo* gave a mixture of the compounds COF_2, FCN, and SiF_4, which condensed at −196 °C, and a mixture of trifluoro- (6.6 g, 49 mmol, 91%) and 6-chloro-3,5-difluoro-1,2,4-triazine (0.4 g, 2.6 mmol, 5%) and a trace of trifluoro-1,3,5-triazine (by i.r. spectroscopy), which condensed at −78 °C. Further trap-to-trap distillation yielded *trifluoro*-1,2,4-*triazine* (Found: C, 26.8; F, 42.6; N, 30.8%; *M*, 135. $C_3F_3N_3$ requires C, 26.7; F, 42.2; N, 31.1%; *M*, 135), as a colourless liquid condensing at −48 °C, with $\lambda_{max.}$ (vapour) 285 and 328 nm, and δ_F 15.9 (F-3, $|^5J|$ 34 Hz), 4.6 (F-5, $|^3J|$ 23 Hz), and −24.9 p.p.m. (6-F), and 6-*chloro*-3,5-*difluoro*-1,2,4-*triazine* (Found: C, 24.1; F, 24.7; N, 27.5%; *M*, 151. $C_3ClF_2N_3$ requires C, 23.8; F, 25.1; N, 27.7%; *M*, 151), as a colourless solid, m.p. 28—30 °C, condensing at 0 °C, with δ_F (melt at 55 °C) 16.5 and 18.3 p.p.m.

Shorter contact times led to increasing amounts of chlorodifluorotriazine, and longer contact time (*ca.* 1.2 s) to lower yields of trifluorotriazine (55%), blackening of the tube, and nitrogen formation.

Nucleophilic Substitution Reactions of Trifluoro-1,2,4-*triazine.*—(*a*) *With water.* To the title triazine (0.69 g, 5.1 mmol), contained in a round-bottomed flask (25 cm³) fitted with a condenser and dropping funnel, was added water (10 cm³) drop by drop. After the resultant exothermic reaction had subsided, the excess of water was removed under reduced pressure, and the remaining solid was recrystallized from water, and sublimed at 150 °C *in vacuo*. to give 6-*fluoro*-1,2,4-*triazine*-3,5(2H,4H)-*dione* (0.31 g, 2.3 mmol, 45%) (Found: C, 27.7; H, 1.4; F, 14.5; N, 32.3%; *M*, 133. $C_3H_2FO_2N_3$ requires C, 27.5; H, 1.5; F, 14.5; N, 32.1%; *M*, 133), as a white solid, m.p. 226—229 °C, $\nu_{max.}$ (mull) 3 150br m, 2 975s, 2 930s, and 2 795m cm⁻¹ (N−H str); δ_F (D_2O) −26.7 p.p.m.

(*b*) *With ammonia.* Gaseous ammonia was bubbled through a solution of the triazine (0.46 g, 3.4 mmol) in tetrahydrofuran (5 cm³), contained in a round-bottomed flask (25 cm³) fitted with a condenser and gas inlet. After the exothermic reaction had subsided, an orange solid was filtered off from a pale yellow solution. The solid was examined by t.l.c., but appeared to be polymeric. The solution was evaporated under reduced pressure, and the resultant solid was recrystallized from ethyl acetate and sublimed at 100 °C *in vacuo* to give 5-*amino*-3,6-*difluoro*-1,2,6-*triazine* (0.34 g, 2.6 mmol, 76%) (Found: C, 27.3; H, 1.6; F, 28.4; N, 42.1%; *M*, 131. $C_3H_2F_2N_4$ requires C, 27.3; H, 1.5; F, 28.8; N, 42.4%; *M*, 131), as a pale yellow solid, m.p. 166 °C (decomp.), $\nu_{max.}$ 3 340m, 3 270m, 3 055s (N−H str.), and 1 668 cm⁻¹ (C=N str.); $\lambda_{max.}$ (ethanol) 274.5 (ϵ 6 600) and 221.5 nm (8 750); δ_H [($CD_3)_2CO$] 7.9 p.p.m.; δ_F 9.2 (3-F, d, ^5J 36 Hz) and −28.1 p.p.m. (6-F).

A reaction carried out in bis(2-methoxyethyl) ether at 100 °C in a sealed tube produced the same 5-aminotriazine.

(*c*) *With 4-chloroaniline.* When a mixture of 4-chloroaniline (2.1 g, 16.5 mmol), trifluoro-1,2,4-triazine (0.65 g, 4.8 mmol), anhydrous sodium carbonate (2.0 g, 19 mmol), and tetrahydrofuran (2 cm³), sealed *in vacuo* in a Pyrex ampoule (70 cm³), was warmed to room temperature, a vigorous exothermic reaction ensued. The yellow precipitate was filtered off, washed with tetrahydrofuran, and the combined solutions in tetrahydrofuran were evaporated to give, after recrystallisation from benzene and light petroleum (b.p. 60—80 °C) and sublimation at 200 °C *in vacuo*, 3,5-*bis*(4-*chloroanilino*)-6-*fluoro*-1,2,4-*triazine* (0.84 g, 2.4 mmol, 50%) (Found: C, 51.1; H, 3.1; Cl, 20.4; F, 5.3; N, 19.7%; *M*, 349. $C_{15}H_{10}Cl_2FN_5$ requires C, 51.4; H, 2.9; Cl, 20.3; F, 5.4; N, 20.0%; *M*, 349) as a pale yellow solid, m.p. 237—239 °C; $\nu_{max.}$ 3 382m, 3 280w, 3 198w, 3 110w, 3 055m sh, 3 025m, 2 885w, 2 850w, and 1 647m cm⁻¹ (C=N str); $\lambda_{max.}$ (in ethanol) 271 (ϵ 28 600); $\lambda_{min.}$ 232 (10 400); $\lambda_{infl.}$ 330 nm (10 700); δ_H 7.86 and 7.37 (AA′BB′-type multiplet), and 7.76 and 7.27 p.p.m. (AA′BB′-type); δ_F −29.3 p.p.m.

(*d*) *With diethylamine.* When a mixture of diethylamine (5.9 g, 81 mmol), the triazine (0.83 g, 6.2 mmol), and anhydrous sodium carbonate (2.0 g, 19 mmol), sealed *in vacuo* in a Pyrex ampoule (70 cm³), was warmed to room temperature, a vigorous reaction ensued. The precipitate was filtered off and washed with diethyl ether. The washings were added to the remaining solution, which was evaporated under reduced pressure to give a dark orange oil. This was distilled at 160—163 °C and 0.2 mmHg to give 3,5-*bis*(*diethylamino*)-6-*fluoro*-1,2,4-*triazine* (0.67 g, 2.8 mmol, 45%) (Found: C, 54.6; H, 8.1; F, 8.0; N, 29.2; *M*, 241. $C_{11}H_{20}FN_5$ requires C, 54.8; H, 8.4; F, 7.9; N, 29.0%; *M*, 241), as a pale orange oil, $\lambda_{max.}$ (in n-hexane) 326 (ϵ 4 313), 264 (6 832), 237 (12 150), and 214 nm (16 350); $\lambda_{min.}$ 298 (2 950), 261 (6 809), and 227 (10 350); $\lambda_{infl.}$ 355 (2 650) and 338 nm (4 223); δ_H 3.3 (CH_2) and 0.9 p.p.m. (CH_3); δ_F −28.1 p.p.m.

Examination of the crude product by g.l.c. and n.m.r. spectroscopy indicated the probable presence of *ca.* 20% of 5-diethylamino-3,6-difluoro-1,2,4-triazine, with δ_F 11.1 (*J* 34 Hz) and −17.2 p.p.m., but this decomposed upon attempted isolation.

(*e*) *With methanol.* A mixture of the triazine (1.38 g, 10.2 mmol), methanol (5 cm³, 124 mmol), and sodium carbonate (2.0 g, 19 mmol), sealed *in vacuo* in a Pyrex ampoule (70 cm³), was warmed to room temperature when a vigorous exothermic reaction gave a white emulsion. The contents of the ampoule were washed out with methanol, filtered, and the methanol removed under reduced pressure to give a white oily solid, which was sublimed at 50 °C *in vacuo* to give a 1 : 2 mixture of 3,5-dimethoxy-6-fluoro- and 5,6-dimethoxy-3-fluoro-1,2,4-triazine (0.66 g, 4.2 mmol, 41%) (Found: C, 37.8; H, 3.6; F, 11.9; N, 26.6%; *M*, 159. Calc. for $C_5H_6FO_2N_3$: C, 37.7; H, 3.8; F, 11.9; N, 26.5%; *M*, 159), with δ_F 9.9 (3-F) and −30.0 p.p.m. (6-F). The moisture-sensitive mixture could not be separated by t.l.c. or g.l.c.

The triazine (1.15 g, 8.5 mmol), methanol (1.22 cm³, 30 mmol), and diethyl ether (5 cm³) reacted vigorously upon being warmed from −78 °C to room temperature to give a clear solution, which was set aside overnight; the solvent was then removed to give a white acidic solid. This was washed with ice-cold aqueous potassium carbonate and

extracted with chloroform. The resulting oil showed three spots on t.l.c. Elution with diethyl ether from a silica column gave, after recrystallisation from light petroleum (b.p. 40—60 °C) trimethoxy-1,2,4-triazine (0.15 g, 0.9 mmol, 10%), m.p. 119—120 °C (lit.,[14] 124—125 °C), which was identified by mass spectrometry.

Dimerisation of Trifluoro-1,2,4-*triazine*.—When trifluoro-1,2,4-triazine (1.0 g, 7.4 mmol) was stored *in vacuo* at −20 °C for 1 month in a Pyrex ampoule, it formed a dark red oil, from which unchanged triazine (0.8 g, 5.9 mmol) was removed. The residue was extracted with chloroform, the solvent removed under reduced pressure, and the residue triturated with light petroleum (b.p. 30—40 °C); it sublimed at 60 °C *in vacuo* and was recrystallised from light petroleum (b.p. 60—80 °C) to give 3,6-*difluoro*-5-(3,5,5,6-*tetrafluoro*-4,5-*dihydro*-1,2,4-*triazin*-4-*yl*)-1,2,4-*triazine* (0.2 g, 0.7 mmol, 20%) (Found: C, 26.5; F, 42.6; N, 31.2%; *M*, 270. $C_6F_6N_6$ requires C, 26.7; F, 42.2; N, 31.1%; *M*, 270), as a white powder, m.p. 60—62 °C, with δ_F 21.2 (CF_2, ^3J 24 Hz), 18.3 (3-F of the dihydrotriazine ring, ^5J 18 Hz), 17.6 (3-F of the triazine ring, ^5J 35 Hz), −12.4 (6-F of the triazine ring), −21.4 (6-F of the dihydrotriazine ring).

Pyrolysis of the Dimer.—The above dimer (0.46 g, 1.7 mmol) was passed over potassium fluoride at 250 °C using the apparatus used to prepare trifluoro-1,2,4-triazine, the flask containing the dimer being heated to 60 °C. The product was collected over 1 h and then fractionated by trap-to-trap distillation *in vacuo* to give trifluoro-1,2,4-triazine (0.42 g, 3.1 mmol, 91%), which condensed at −78 °C, and small amounts of carbonyl fluoride and silicon tetrafluoride.

Pyrolysis of Trifluoro-1,2,4-*triazine*.—The triazine (1.1 g, 8.1 mmol) was passed at *ca.* 1 mmHg through a silica tube (10 mm i.d., heated length 350 mm) packed with silica chips and heated to 800 °C during 1 h. The product, which was collected in a trap cooled to −196 °C, was fractionated by trap-to-trap distillation *in vacuo* to give a mixture of cyanogen fluoride, carbonyl fluoride, and silicon tetrafluoride, which condensed at −196 °C and was identified by i.r. spectroscopy, unchanged trifluoro-1,2,4-triazine (0.9 g, 6.6 mmol, 82%), which condensed at −78 °C and contained traces of trifluoro-1,3,5-triazine by i.r. spectroscopy, and

traces of a pale yellow oil, which condensed at 0 °C and was tentatively identified as 3,6-difluoro-5-isocyanato-1,2,4-triazine, $\nu_{max.}$ 2 250 cm⁻¹ (N=C=O str.), $M^{+\cdot}$, 158 (Calc. for $C_4F_2ON_4$: *M*, 158).

Photolysis of Trifluoro-1,2,4-*triazine*.—The triazine, sealed *in vacuo* in a silica tube, was recovered unchanged (91%), after irradiation for 163 h with light from a Hanovia UVS 500 lamp at a distance of 7 cm.

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