

Polyhalogenonitrobenzenes and derived compounds

Part 5. Improved preparations of 1,2,3,4-tetrafluoro-5,6-dinitrobenzene and 3,4,5,6-tetrafluoro-1,2-phenylenediamine, and the use of the latter for the synthesis of tetrafluorobenzheterocycles ¹

Alan Heaton ^{a,*}, Mark Hill ^{a,2}, Frederick Drakesmith ^b

^a School of Chemical and Physical Sciences Liverpool John Moores University, Byrom Street, Liverpool L3 3AF, UK

^b EA Technology Ltd., Capenhurst, Chester CH1 6ES, UK

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Abstract

The preparation of 2,3,4,5-tetrafluoro-6-nitroaniline (**3**) by amination of pentafluoronitrobenzene has been speeded up, scaled up and the yield increased by controlling the reaction by TLC monitoring and using 'dry column' chromatography. Compound (**3**) was readily converted to 1,2,3,4-tetrafluoro-5,6-dinitrobenzene (**2**) by peroxytrifluoroacetic acid and to 3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**) by SnCl₂/HCl. Compound (**1**) was shown to be a versatile intermediate for the synthesis of tetrafluoro-benzimidazoles, -triazoles and -quinoxalines. The fungicidal activity of the latter are reported here.

Keywords: Polyhalogenonitrobenzenes; Synthesis; Chromatography

1. Introduction

In the preceding paper [1] we described our attempts to prepare 1,2,3,4-tetrafluoro-5,6-dinitrobenzene (TFDNB) (**2**) from its chlorine analogue (TCDNB) by halogen exchange using potassium fluoride under a variety of conditions, solvents etc. Unfortunately this was unsuccessful with brown fumes being evolved, which indicated loss of the nitro-group(s). Interestingly, however, the products of these reactions were pentachloronitrobenzene and pentachlorofluorobenzene.

There are two published routes to TFDNB. The first is a six stage synthesis starting from 1,2,3,4-tetrafluorobenzene (TFB) [2]. In contrast to 1,2,3,4-tetrachlorobenzene, TFB cannot be dinitrated. Thus an indirect route comprising a first mononitration stage followed by five further steps is employed.

We therefore switched our attention to the second published route [3] which is shown in Scheme 1. The disadvantages of this method are (i) relatively expensive starting material, (ii) separation of the desired 2,3,4,5-tetrafluoro-6-nitroaniline (**3**) from the other three products formed in the first step by column chromatography, and the limitations that this imposes on the scale and speed of operation. We have been able to considerably reduce the latter problems as follows.

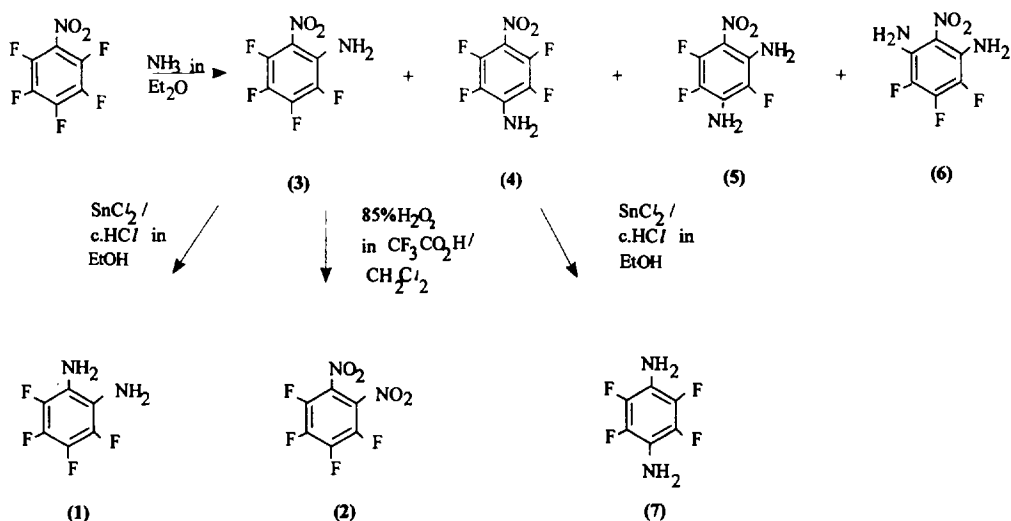
Firstly, by following the amination of pentafluoronitrobenzene by TLC, the reaction can be stopped at the stage where only one fluorine is displaced, i.e. no. (**5**) or (**6**) are formed. Moreover the isomeric products (**3**) and (**4**) are still formed in the ratio of 7:3. This simplifies the chromatographic separation to isolate (**3**), which has also been improved. We have achieved this by using 'dry column' chromatography [4,5]. This is not only quicker than traditional (liquid flow) column chromatography but it also uses less solvent. We have also been able to scale up the process by successfully separating 10 g of a mixture of (**3**) and (**4**), as detailed in the experimental section. Thus we have been able to scale up, speed up and increase the yield in the preparation of (**3**).

Compound (**3**) was readily reduced by tin (II) chloride, and hydrochloric acid in ethanol to the title compound,

* Corresponding author. Present address: School of Pharmacy and Chemistry, Liverpool John Moores University, Byrom Street, Liverpool L3 3AF, UK.

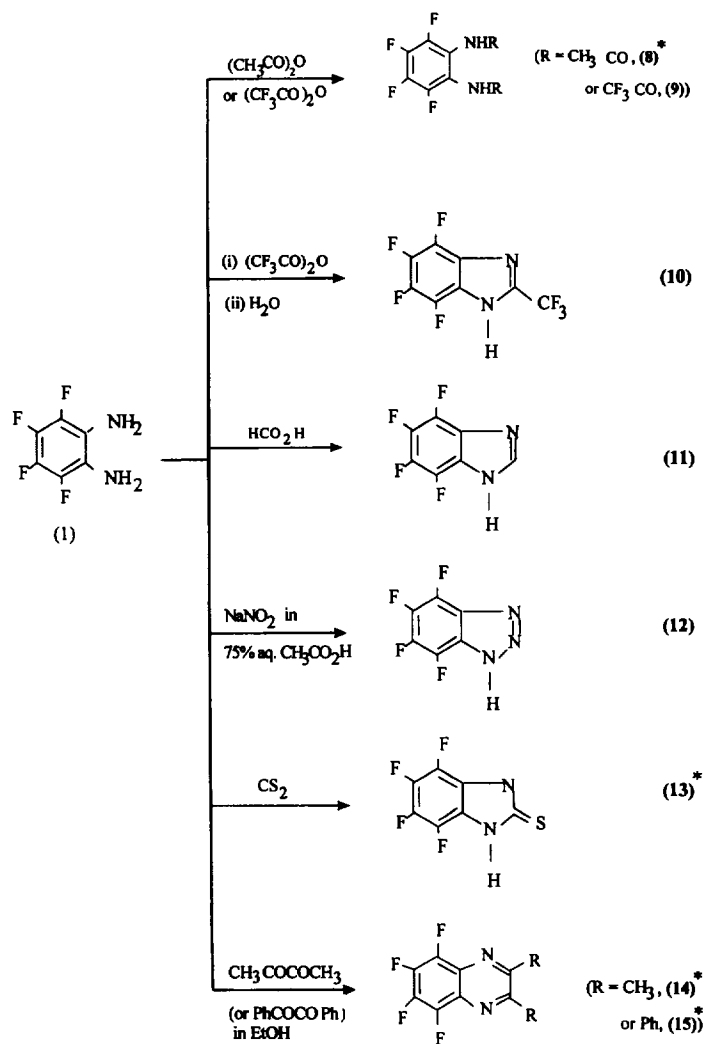
¹ Part 4: Alan Heaton, Mark G. Hill and Frederick G. Drakesmith, preceding paper.

² Present address: Kodak Ltd., Acomfield Road, Kirkby, Liverpool, L33 7UF, UK.



3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**) in 64% yield. This reduction had previously been achieved in 77% yield by catalytic hydrogenation. The 1,2-diamine system allows nitrogen containing heterocyclic rings to be built onto the

fluorinated benzene ring. We have been able to demonstrate the versatility of (**1**) as an intermediate for the formation of these tetrafluorobenzheterocycles by carrying out the reactions shown in Scheme 2. Note that although some of these



products have previously been reported, others are new compounds (indicated by *) and the pesticidal activity of some of these is reported below. These reactions clearly demonstrate what a versatile intermediate 3,4,5,6-tetrafluoro-1,2-phenylenediamine is for the synthesis of a variety of tetrafluorobenzheterocycles-benzimidazoles, benzotriazoles and quinoxalines.

The isomeric 2,3,5,6-tetrafluoro-4-nitroaniline (**4**) which is formed in the amination of pentafluoronitrobenzene along with (**3**), has also been reduced to the corresponding diamine (**7**) and this has been characterised by formation of its *N,N'*-bis (trifluoroacetyl) derivative.

The *in vivo* fungicidal activity of compounds (**4**), (**7**), (**8**), (**9**) against several plant diseases was determined by simultaneous foliar and soil applications to appropriate host plants at a combined application rate of 500 ppm and the responses observed were as follows. All were inactive against *Pyricularia oryzae* and only (**15**) was active against *Erysiphe graminis* where it showed a control rate in the range 20%–34%. Compound (**4**) was the only one active against *Puccinia recondita* 35%–44% control. This compound was also the only one active against *Plasmopora viticola*, where it gave 65%–74% control.

2,3,4,5-Tetrafluoro-6-nitroaniline (**3**) was successfully oxidised to TFDNB (**2**) on a 100 mg scale with peroxydisulphuric acid but when this was scaled up to a 1 g scale violent gassing occurred and most of the product was lost.

However the conversion was successfully achieved on a 10.5 g scale using peroxytrifluoroacetic acid.

2. Experimental

Infrared spectra were recorded as potassium bromide discs using a Unicam SP 1000 instrument.

Mass spectra were recorded on a V.G. Micromass 16B or on a MS30 instrument.

G.C./Mass spectra were recorded on a Finigan MAT 1020 Automated G.C./M.S. instrument.

2.1. Preparation of 2,3,4,5-tetrafluoro-6-nitroaniline (**3**)

Dry ammonia gas was passed through a solution of pentafluoronitrobenzene (10.0 g; 0.0469 mol) in diethyl ether (300 cm³) at room temperature for 3 h. The mixture was stirred for a further 18 h and then filtered to remove the precipitated ammonium fluoride. The filtrate was then washed with water, dried over anhydrous MgSO₄ and filtered. Removal of the solvent under reduced pressure gave a red solid which was purified by dry column chromatography (silica 100–120 mesh; toluene/60–80 petrol, 50:50) to give four fractions.

Solvents were removed from the first fraction under reduced pressure to give a yellow solid which was recrystallised from hot 60–80 petrol to give the yellow 2,3,4,5-tetra-

fluoro-6-nitroaniline (**3**), (6.5 g; 66%) mpt. 41–43 °C (cf. lit. 42.5–43.5 °C) [3].

The infrared spectrum of this compound shows two characteristic N–H stretching absorptions at 3500 cm⁻¹ and 3395 cm⁻¹ and two C–NO₂ absorptions at 1549 cm⁻¹ and 1352 cm⁻¹.

Removal of the solvents from the second fraction gave a yellow solid which was recrystallised from hot 60–80 petrol to give the yellow 2,3,5,6-tetrafluoro-4-nitroaniline, (**4**), (2.2 g; 22%) mpt. 106–108 °C (cf lit. 106.5–108 °C) [3]. The infrared spectrum of this compound shows two characteristic N–H stretching absorptions at 3482 cm⁻¹ and 3380 cm⁻¹ and two C–NO₂ absorptions at 1535 cm⁻¹ and 1330 cm⁻¹.

The solvents were removed from the third fraction under reduced pressure to give a red solid which was recrystallised from hot 60–80 petrol to give red needles of 4,5,6-trifluoro-2-nitro-1,3-phenylenediamine, (**6**), (0.15 g; 1.5%) mpt. 160–162 °C (cf lit. 162–163.5 °C). [3].

The infrared spectrum of this compound shows three characteristic N–H stretching absorptions at 3470 cm⁻¹, 3370 cm⁻¹ and 3320 cm⁻¹ and two C–NO₂ absorptions at 1535 cm⁻¹ and 1360 cm⁻¹.

Removal of the solvents from the fourth fraction gave a yellow solid which was recrystallised from hot 60–80 petrol to give bright yellow crystals of 2,4,5-trifluoro-6-nitro-1,3-phenylenediamine (**5**) (0.23 g; 2.4%) mpt. 146–148 °C (cf. lit. 146.5–148 °C) [3].

The infrared spectrum of this compound shows five characteristic N–H stretching absorptions at 3500 cm⁻¹, 3440 cm⁻¹, 3390 cm⁻¹, 3330 cm⁻¹ and 3220 cm⁻¹ and two C–NO₂ absorptions at 1520 cm⁻¹ and 1370 cm⁻¹.

When this reaction was repeated at room temperature for 1.5 h, purification of the product mixture by dry column chromatography gave two fractions.

Removal of the solvent from the first fraction gave a yellow solid which was recrystallised from hot 60–80 petrol to give the yellow 2,3,4,5-tetrafluoro-6-nitroaniline, (**3**), (6.6 g; 67%) mpt. 41–43 °C.

The solvents were removed from the second fraction to give a yellow solid which was recrystallised from hot 60–80 petrol to give the pale yellow 2,3,5,6-tetrafluoro-4-nitroaniline, (**4**), (2.7 g; 27%) mpt. 106–108 °C.

2.2. Preparation of 1,2,3,4-tetrafluoro-5,6-dinitrobenzene (TFDNB), (**2**)

2.2.1. (1) Oxidation of 2,3,4,5-tetrafluoro-6-nitroaniline using peroxydisulphuric acid

2,3,4,5-Tetrafluoro-6-nitroaniline (**3**), (100 mg; 0.000476 mol) was dissolved in concentrated sulphuric acid (6 cm³) and cooled in an ice bath. Hydrogen peroxide (2.2 cm³ of a 30% w/v solution; 0.0194 mol) was slowly added to the magnetically stirred solution. The mixture was stirred and heated at 50 °C for 4 h.

After cooling in an ice bath, distilled water (10 cm³) was added and the aqueous solution was extracted with dichlo-

romethane ($2 \times 10 \text{ cm}^3$). The combined extracts were dried over anhydrous MgSO_4 , filtered and the solvent was removed under reduced pressure to give the pale yellow 1,2,3,4-tetrafluoro-5,6-dinitrobenzene (**2**), (0.06 g; 53%) mpt. 27–30 °C (cf lit. 31–33 °C). [2,6].

The infrared spectrum of this compound shows two C– NO_2 absorptions at 1580 cm^{-1} and 1350 cm^{-1} .

This compound was found (t.l.c., g.l.c., i.r) to be identical to an authentic sample of TFDNB.

When this reaction was repeated on a larger scale (using 1.0 g of 2,3,4,5-tetrafluoro-6-nitroaniline), violent gassing occurred during the reaction and most of the product was lost.

After work-up, TFDNB was obtained in approximately 10% yield.

2.2.2. (II) Oxidation of 2,3,4,5-tetrafluoro-6-nitroaniline (**3**), using peroxytrifluoroacetic acid

Hydrogen peroxide (19 cm^3 of an 85% aqueous solution) was added to dichloromethane (60 cm^3) in a 500 ml R.B. flask. The flask was cooled in an ice bath and trifluoroacetic acid (39.0 g; 0.342 mol) was slowly added with stirring. A solution of 2,3,4,5-tetrafluoro-6-nitroaniline (10.5 g; 0.05 mol) in dichloromethane (30 cm^3) was added to the oxidising mixture over 45 min during which the colour of the mixture changed from yellow to green. The mixture was then stirred for 16 h at room temperature and then heated to reflux temperature and maintained under reflux conditions for a further two hours. After cooling, distilled water (100 cm^3) was added and the organic phase was separated and washed with distilled water. The solution was dried over anhydrous MgSO_4 , filtered, and removal of the solvent under reduced pressure gave a green viscous oil. The crude product (9.4 g; 82.5%) was purified by distillation (89°C/0.9 mm Hg) to give a pale green oil which on cooling gave the pale green 1,2,3,4-tetrafluoro-5,6-dinitrobenzene (**2**), mpt. 30–32 °C.

2.3. Preparation of 3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**)

2,3,4,5-Tetrafluoro-6-nitroaniline (**3**), (10.0 g; 0.0476 mol) was added slowly to a refluxing mixture of tin (II) chloride (88 g; 0.464 mol), concentrated hydrochloric acid (d.1.18, 114 g; 3.123 mol) and dried ethanol (57.4 g; 1.248 mol), and the reflux was continued for a further 30 min. Water (150 cm^3) was then added and the solution was allowed to cool. The solution was neutralised using sodium bicarbonate and the precipitated inorganic salts were filtered off and washed with dichloromethane. The filtrate was extracted with dichloromethane and the combined extracts and washings were dried over anhydrous MgSO_4 and filtered. Removal of the solvent under reduced pressure gave a white solid which was recrystallised from 60–80 petrol to give white needles of 3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**), (5.5g; 64%) mpt. 130–131 °C (cf lit. 131–131.5 °C) [2,3].

The infrared spectrum of this compound shows two characteristic N–H stretching absorptions at 3440 cm^{-1} and 3355 cm^{-1} .

The mass spectrum of this compound shows the M^+ ion at 180.

| | C | H | N | F |
|---|-------|------|-------|-------|
| Calculated for $\text{C}_6\text{H}_4\text{F}_4\text{N}_2$ | 40.00 | 2.22 | 15.56 | 42.22 |
| Found: | 39.95 | 2.22 | 15.58 | 42.38 |

2.4. Cyclisation reactions of 3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**)

2.4.1. Formic acid

3,4,5,6-Tetrafluoro-1,2-phenylenediamine (**1**), (200 mg; 0.00111 mol) was heated under reflux conditions for 3 h with 98% formic acid (7 cm^3). The reaction mixture was taken up in an excess of 10% aqueous sodium hydroxide and filtered. The product was liberated from the filtrate by acidification to give a pale yellow solid which was recrystallised from hot methanol to give the white 4,5,6,7-tetrafluorobenzimidazole, (**11**), (150 mg; 71%) mpt. 232–233 °C.

The infrared spectrum of this compound shows an N–H stretching absorption at 3120 cm^{-1} and an absorption at 1555 cm^{-1} believed to be owing to an N=C–H vibration.

The mass spectrum of this compound shows the M^+ ion at 190.

| | C | H | N |
|---|-------|------|-------|
| Calculated for $\text{C}_7\text{H}_2\text{F}_4\text{N}_2$ | 44.21 | 1.05 | 14.74 |
| Found: | 43.99 | 1.88 | 14.43 |

2.4.2. Acetic anhydride

3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**), (100 mg; 0.000555 mol) was heated under reflux conditions for 2 h in acetic anhydride (3 cm^3). Water (5 cm^3) was added and reflux was continued for a further 30 min.

Concentrated ammonia solution was added and, on cooling, a white precipitate was formed which was filtered at the pump. The crude product was recrystallised from 60–80 petrol to give white needles of *N,N'*-bis-(acetyl)-3,4,5,6-tetrafluoro-1,2-phenylenediamine (**8**), (76 mg; 52%) mpt. 214–216 °C.

The infrared spectrum of this compound shows a broad N–H stretching absorption at 3200 cm^{-1} , three aliphatic C–H stretching absorptions at 2980 cm^{-1} , 2960 cm^{-1} and 2930 cm^{-1} , and a C=O stretching absorption at 1680 cm^{-1} .

The mass spectrum of this compound shows the M^+ ion at 264.

| | C | H | N | F |
|--|-------|------|-------|-------|
| Calculated for $\text{C}_{10}\text{H}_8\text{F}_4\text{N}_2\text{O}_2$ | 45.45 | 3.03 | 10.61 | 28.79 |
| Found: | 45.91 | 2.86 | 10.64 | 29.84 |

2.4.3. Trifluoroacetic anhydride

(I) 3,4,5,6-tetrafluoro-1,2-phenylenediamine, (**1**) (100 mg; 0.000555 mol) was heated under reflux conditions for 2 h in trifluoroacetic anhydride (0.75 cm³). Excess trifluoroacetic anhydride was removed by co-distillation with carbon tetrachloride to leave a white solid. The product was recrystallised from toluene/60–80 petrol (20:80) to give the white *N,N'*-bis(trifluoroacetyl)-3,4,5,6-tetrafluoro-1,2-phenylenediamine (**9**), (179 mg; 87%) mpt. 166–167 °C (cf lit. 165–167 °C) [2,3].

The infrared spectrum of the compound shows two N–H stretching absorptions at 3280 cm⁻¹ and 3220 cm⁻¹, and a C=O stretching absorption at 1720 cm⁻¹.

The mass spectrum of this compound shows the M⁺ ion at 372.

| | C | H | N | F |
|---|-------|------|------|-------|
| Calculated for C ₁₀ H ₂ F ₁₀ N ₂ O ₂ | 32.25 | 0.54 | 7.53 | 51.08 |
| Found: | 31.15 | 0.86 | 7.48 | 50.72 |

(II) 3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**), (100 mg; 0.000555 mol) was heated under reflux conditions for 2 h in trifluoroacetic anhydride (0.75 cm³) and then excess trifluoroacetic anhydride was removed by co-distillation with carbon tetrachloride. The resulting white solid was refluxed in water (5 cm³) for 30 min and then an excess of concentrated ammonia solution was added.

After cooling, the aqueous solution was extracted with diethyl ether and the combined extracts were dried over anhydrous MgSO₄ and filtered.

Removal of the solvent under reduced pressure gave a white solid which was recrystallised from 60–80 petrol, to which a small amount of toluene had been added, to give the white 4,5,6,7-tetrafluoro-2-trifluoromethylbenzimidazole (**10**), (80 mg; 56%) mpt. 161–162 °C (cf. lit. 163–163.5 °C) [3].

The infrared spectrum of this compound shows a characteristic N–H stretching absorption at 3420 cm⁻¹ and several absorptions in the 1300–1100 cm⁻¹ region, believed to be due to C–F stretching absorptions.

The mass spectrum of this compound shows the M⁺ ion at 258.

| | C | H | N | F |
|--|-------|------|-------|-------|
| Calculated for C ₈ HF ₇ N ₂ | 37.21 | 0.39 | 10.85 | 51.55 |
| Found: | 37.59 | 0.56 | 10.58 | 50.00 |

2.4.4. Carbon disulphide

3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**), (250 mg; 0.00139 mol) was added to a solution of carbon disulphide (1.06 g; 0.0139 mol) in D.M.F. (8 cm³).

The solution was magnetically stirred at 50–55 °C for 24 h, cooled and then poured into an excess of water. Unreacted carbon disulphide was allowed to evaporate off and the precipitate was filtered off. The product was recrystallised from aqueous methanol to give the pale yellow 4,5,6,7-tetrafluoro-

robenzimidazole-2-thione (**13**), (262 mg; 85%) mpt. > 350 °C.

The infrared spectrum of this compound shows two N–H stretching absorptions at 3280 cm⁻¹ and 3210 cm⁻¹ and two absorptions at 1553 cm⁻¹ and 1490 cm⁻¹ believed to be due to a C=S (linked to N) stretching vibration.

The mass spectrum of this compound shows the M⁺ ion at 222.

2.4.5. Nitrous acid

A solution of 3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**), (100 mg; 0.000555 mol) in 75% aqueous acetic acid (5 cm³) was cooled in an ice bath and sodium nitrite (84 mg; 0.00122 mol) in a little water was added. The resulting yellow solution was heated at 70 °C for 30 min. Water (10 cm³) was added and the aqueous solution was extracted using dichloromethane. The combined extracts were dried over anhydrous MgSO₄, filtered, and removal of the solvent under reduced pressure gave a pale yellow solid. The crude product was recrystallised from methanol to give the white 4,5,6,7-tetrafluorobenzotriazole (**12**), (80 mg; 75%) mpt. 172.5–174 °C (cf lit. 162.5 °C) [7].

The infrared spectrum of this compound shows a very broad absorption between 3180 cm⁻¹ and 2200 cm⁻¹.

The mass spectrum of this compound shows the M⁺ ion at 191.

| | C | H | N | F |
|--|-------|------|-------|-------|
| Calculated for C ₆ HF ₄ N ₃ | 37.70 | 0.52 | 21.99 | 39.79 |
| Found: | 38.15 | 0.74 | 21.95 | 39.50 |

2.4.6. Diacetyl

3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**), (250 mg; 0.00139 mol) was added to a solution of diacetyl (143 mg; 0.00166 mol) in dried ethanol (6 cm³). The solution was heated under reflux conditions for 2 h. On cooling, a white precipitate was formed which was filtered off and recrystallised from hot ethanol to give white crystals of 5,6,7,8-tetrafluoro-2,3-dimethylquinoxaline (**14**), (220 mg; 78%) mpt. 109–110 °C.

The infrared spectrum of this compound shows two aliphatic C–H stretching absorptions at 2965 cm⁻¹ and 2930 cm⁻¹, and a C=N stretching absorption at 1657 cm⁻¹.

The mass spectrum of this compound shows the M⁺ ion at 230.

| | C | H | N | F |
|---|-------|------|-------|-------|
| Calculated for C ₁₀ H ₆ F ₄ N ₂ | 52.17 | 2.61 | 12.17 | 33.05 |
| Found: | 52.15 | 2.89 | 12.12 | 32.50 |

2.4.7. Benzil

3,4,5,6-tetrafluoro-1,2-phenylenediamine (**1**), (250 mg; 0.00139 mol) was added to a solution of benzil (435 mg; 0.00207 mol) in ethanol (6 cm³). The solution was heated under reflux conditions for 18 h; during the reaction, needle-like crystals were formed. After cooling, the crude product

was filtered off and recrystallised from hot ethanol to give white crystals of 5,6,7,8-tetrafluoro-2,3-diphenylquinoxaline (**15**), (450 mg; 92%) mpt. 188–189 °C.

The infrared spectrum of this compound shows two aromatic C–H stretching absorptions at 3090 cm^{-1} and 3060 cm^{-1} and a C=N stretching absorption at 1657 cm^{-1} .

The mass spectrum of this compound shows the M^+ ion at 354.

| | C | H | N | F |
|---|-------|------|------|-------|
| Calculated for $\text{C}_{20}\text{H}_{10}\text{F}_4\text{N}_2$ | 67.80 | 2.82 | 7.91 | 21.47 |
| Found: | 67.59 | 2.93 | 7.96 | 21.66 |

2.5. Preparation of 2,3,5,6-tetrafluoro-1,4-phenylenediamine (**7**)

2,3,5,6-tetrafluoro-4-nitroaniline (**5**), (1.87 g; 0.0089 mol) was slowly added to a refluxing mixture of tin (II) chloride (16.5 g; 0.0873 mol), concentrated hydrochloric acid (d 1.18, 21.4 g; 0.586 mol) and dried ethanol (10.8 g), and the reflux was continued for a further 30 min. Water (30 cm^3) was then added and the solution was allowed to cool.

The aqueous solution was then neutralised using sodium bicarbonate and the precipitated inorganic salts were filtered off and washed with dichloromethane.

The filtrate was extracted with dichloromethane and the combine extracts and washings were dried over anhydrous MgSO_4 and filtered. Removal of the solvent under reduced pressure gave a white solid which was recrystallised from 60–80 petrol to give white needles of 2,3,5,6-tetrafluoro-1,4-phenylenediamine (**7**), (1.0 g; 63%) mpt. 144–145 °C (cf lit. 143.5–144 °C) [3].

The infrared spectrum of this compound shows three N–H stretching absorptions at 3440 cm^{-1} , 3360 cm^{-1} and 3210 cm^{-1} .

The mass spectrum of this compound shows the M^+ ion at 180.

2.6. Reaction of 2,3,5,6-tetrafluoro-1,4-phenylenediamine (**7**), with trifluoroacetic anhydride

2,3,5,6-tetrafluoro-1,4-phenylenediamine (**7**), (0.4 g; 0.0222 mol) was heated under reflux conditions for two hours in trifluoroacetic anhydride (3 cm^3). Excess trifluoroacetic anhydride was removed by co-distillation with carbon tetrachloride to leave a white solid. The crude product was recrystallised from aqueous ethanol to give the white *N,N'*-bis(trifluoroacetyl)-2,3,5,6-tetrafluoro-1,4-phenylenediamine (0.78 g; 94%) mpt. 274–275 °C (cf. lit. 274.5–275 °C) [3].

The infrared spectrum of this compound shows an N–H stretching absorption at 3252 cm^{-1} and two C=O stretching absorptions at 1744 cm^{-1} and 1725 cm^{-1} .

The mass spectrum of this compound shows the M^+ ion at 372.

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