

## THE ELECTROCHEMICAL OXIDATION OF POLYFLUOROAROMATIC AMINES—III THE SYNTHESIS OF POLYFLUOROACRIDONES

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**Abstract**—Electrochemical oxidation of 2-amino-nona- and 2-amino-2',3',4',5',6'-penta-fluorobenzophenone at a platinum anode gave octa- and 1,2,3,4-tetra-fluoroacridone respectively. 2-Amino-nona-fluorobenzophenone was prepared by reduction of the nitro-benzophenone, obtained by nitration of 2-H-nona-fluorobenzophenone. Reduction of the nitro compound also gave perfluoro-3-phenylanthranil which was converted to octafluoroacridone by pyrolysis.

ELECTROCHEMICAL oxidation of amino-polyfluorodiphenylamines affords octa- and tetrafluorophenazine and substituted polyfluorophenazines. We now describe the application of this method to aminopolyfluorobenzophenones to give octa- and tetra-fluoroacridone.

The starting material for octafluoroacridone was 2H-nonafluorobenzhydrol made by the reaction of 1,2,3,4-tetrafluorophenyl magnesium bromide with pentafluorobenzaldehyde. Oxidation of this benzhydrol with chromium trioxide gave 2H-nonafluorobenzophenone. The structure of these two compounds was confirmed by  $^{19}\text{F}$  NMR and IR spectroscopy. Nitration of 2H-nonafluorobenzophenone was effected using fuming nitric acid in sulpholane containing  $\text{BF}_3$  or in conc.  $\text{H}_2\text{SO}_4$ , the latter system being the more reactive. Nitrations of other hydrogen-containing polyfluoroaromatics have been described.<sup>2</sup>

Reduction of the 2-nitrononafluorobenzophenone with a Pd/C catalyst gave a mixture of two compounds. The major component was identified as 2-amino-nonafluorobenzophenone by chemical analysis and spectrographic methods. The second component was found to be nonafluoro-3-phenyl anthranil arising via interaction with the CO group. Reduction of 2-nitro-nonafluorobenzophenone with stannous chloride/HCl in ethanol gave only the anthranil. 3-Pentafluorophenyl anthranil was formed<sup>3</sup> by reduction of 2,3,4,5,6-pentafluoro-2'-nitro-benzophenone using zinc in ethanolic ammonium chloride, a known method for preparation of anthranils.<sup>3</sup>

Electrolytic oxidation of the amino-phenone at +1.55 – +1.60 V (*vs* SCE) gave octafluoroacridone, a yellow solid, m.p. 282–284° (with dec), with a UV spectrum in ethanol very similar to those of acridone<sup>4</sup> and tetrafluoroacridone.<sup>3</sup> Octafluoroacridone was also obtained by the pyrolysis of nonafluoro-3-phenyl-anthranil (cf 1,2,3,4-tetrafluoroacridone from<sup>3</sup> 3-pentafluorophenylanthranil).

1,2,3,4-Tetrafluoroacridone was obtained in low yield by electrochemical oxidation of 2-amino-2',3',4',5',6'-pentafluorobenzophenone<sup>3</sup> at +1.4 – +1.5 V (*vs* SCE),

the sample obtained being identical with that from the alternative route.<sup>3</sup> Further experiments showed that the tetrafluoroacridone itself was susceptible to electrochemical oxidation at the potentials used for the oxidation of the parent amine.

### EXPERIMENTAL

The apparatus and technique for electrochemical oxidation were as previously described.<sup>1</sup> NMR spectra were recorded on samples dissolved in deuteroacetone unless otherwise stated. All data are quoted on the  $\delta$  scale with high field (low frequency) shifts negative, the reference standards ( $\delta = 0.0$ ) being TMS and  $\text{CCl}_3\text{F}$  for  $^1\text{H}$  and  $^{19}\text{F}$  spectra respectively.

#### 2H-Nonafluorobenzhydrol

To 1,2,3,4-tetrafluorobromobenzene<sup>5</sup> (8.0 g) in dry ether (50 ml) was added dry Mg (0.85 g) and the mixed warmed and stirred for 3 hr. The soln was cooled to  $0^\circ$ , pentafluorobenzaldehyde (6.4 g) in dry ether (20 ml) added and the mixture stirred under reflux for 2 h. The soln was acidified with 4N HCl and the ether layer separated. The aqueous layer was extracted with ether ( $2 \times 50$  ml) and the combined ethereal solns dried ( $\text{MgSO}_4$ ) and evaporated. Vacuum distillation of the residue gave (i) pentafluorobenzaldehyde (1.2 g) and (ii) a white solid (5.8 g), b.p.  $94\text{--}95^\circ/0.02$  mm. Recrystallization from light petroleum (b.p.  $60\text{--}80^\circ$ ) gave 2H-nonafluorobenzhydrol (2.77 g), m.p.  $92.5\text{--}93^\circ$ . (Found: C, 45.2; H, 1.1; F, 49.1;  $\text{C}_{13}\text{H}_3\text{F}_9\text{O}$  requires: C, 45.1; H, 0.87; F, 49.5%). Mass spectrometry gave a top mass peak 346 in agreement with the empirical formula. The  $^1\text{H}$  NMR spectrum consisted of three signals intensity ratio 1:1:1 with chemical shifts  $\delta$  7.35 to 7.75 (m), 6.35 (s) and 5.05 (broad s). The  $^{19}\text{F}$  spectrum gave six signals at  $\delta$   $-139.3$ ,  $-143.1$ ,  $-143.9$  (all m's),  $-155.4$  (tr of tr's),  $-157.5$  and  $-162.7$  (both m's) with intensity ratio 1:2:1:1:2:2 respectively, in agreement with the assigned structure.

#### 2H-Nonafluorobenzophenone

Chromium trioxide (4.5 g) 2H-nonafluorobenzhydrol (5.3 g) and glacial AcOH (50 ml) were refluxed for 30 min and the mixture poured into excess water. The soln was then extracted with ether ( $3 \times 100$  ml), the ether extracts washed with  $\text{NaHCO}_3$  aq, dried ( $\text{MgSO}_4$ ), and evaporated to yield a colourless oil (3.5 g) which crystallized on standing. Recrystallization gave 2-H-nonafluorobenzophenone (2.49 g) m.p.  $46^\circ$ . (Found: C, 45.1; H, 0.3; F, 49.7;  $\text{C}_{13}\text{HF}_9\text{O}$  requires: C, 45.3; H, 0.3; F, 49.7%). Mass spectrometry gave a top mass peak of 344 as required. The  $^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ) showed one signal  $\delta$  7.35–7.85 (m). The  $^{19}\text{F}$  spectrum consisted of seven signals at  $\delta$   $-136.0$ ,  $-137.7$ ,  $-141.9$ ,  $-144.1$  (all m's respectively). The IR spectrum showed a strong absorption at  $1690\text{ cm}^{-1}$  ( $> \text{C}=\text{O}$ ) and a weak absorption at  $3100\text{ cm}^{-1}$  (aryl H).

#### 2-Nitro-nonafluorobenzophenone

(i) *Sulpholane*. A mixture of sulpholane (20 ml) and fuming  $\text{HNO}_3$  (1.0 ml) was saturated with  $\text{BF}_3$  at  $0^\circ$ . 2-H-nonafluorobenzophenone (3.0 g) was added and the mixture heated to  $70^\circ$  for  $3\frac{1}{2}$  h with stirring. The mixture was poured onto crushed ice and extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 100$  ml). The organic layers were combined, dried ( $\text{MgSO}_4$ ) and evaporated to yield a product (3.1 g), which was shown by TLC to be a two component mixture. Separation by column chromatography (silica gel, light petroleum b.p.  $40\text{--}60^\circ$ :  $\text{C}_6\text{H}_6 = 3:1$  eluant) gave 2-H-nonafluorobenzophenone (1.4 g) and a second product (1.3 g). Recrystallization (EtOH) gave 2-nitro-nonafluorobenzophenone (0.7 g) m.p.  $109.5\text{--}110^\circ$ . (Found: C, 40.1; H, 0.4; N, 3.4; F, 43.9.  $\text{C}_{13}\text{F}_9\text{NO}_3$  requires: C, 40.1; H, 0.0; N, 3.6; F, 44.0%). Mass spectrometry gave a top mass peak of 389 (required). The  $^{19}\text{F}$  NMR spectrum consisted of 6 signals at  $\delta$   $-138.7$ ,  $-140.5$  (both m's),  $-141.8$  (d of tri),  $-145.3$ ,  $-146.8$  (both m's) and  $-160.6$  (tr of d's) with intensity ratios 1:2:1:2:1:2 respectively. The IR spectrum showed absorptions at  $1700\text{ cm}^{-1}$  ( $> \text{C}=\text{O}$ ) and approximately  $1500\text{ cm}^{-1}$  (fluoroaromatic ring).

(ii) *Conc.  $\text{H}_2\text{SO}_4$* . The phenone (1.3 g) was dissolved in conc  $\text{H}_2\text{SO}_4$  (5 ml) and heated to  $65^\circ$  when a mixture of fuming  $\text{HNO}_3$  (4 ml) and conc  $\text{H}_2\text{SO}_4$  (4 ml) was added slowly. The temp of the mixture was raised to  $90^\circ$  and maintained for 2 h. The soln was cooled, poured into crushed ice (200 g) and the mixture extracted with ether ( $3 \times 50$  ml). The ethereal extracts were dried ( $\text{MgSO}_4$ ) and evaporated to yield 2-nitro-nonafluorobenzophenone (0.7 g).

#### Reduction of 2-nitro-nonafluorobenzophenone

(i) *Hydrogenation.* To 2-nitro-nonafluorobenzophenone (1.3 g) in EtOH (70 ml) was added Pd/Charcoal (0.1 g, 10% Pd) and the mixture hydrogenated. The suspension was filtered and the EtOH evaporated to give a yellow solid (1.1 g). Separation by column chromatography (silica gel, light petroleum b.p. 40–60°: C<sub>6</sub>H<sub>6</sub> = 3:1 eluant) gave (i) component A (0.3 g) and (ii) component B (0.5 g).

Component A (0.3 g) recrystallized from CCl<sub>4</sub> to give *perfluoro-3-phenyl-anthranil* (0.24 g) m.p. 125–126°. (Found: C, 43.5; N, 4.0; F, 48.0. C<sub>13</sub>F<sub>9</sub>NO requires: C, 43.7; N, 3.9; F, 48.0%). Mass spectrometry gave a top mass peak of 357 (required). The <sup>19</sup>F NMR spectrum consisted of 6 signals with chemical shifts  $\delta$  –137.9, –147.2 (both m's), –148.6 (tr), –153.7 (m), –156.1 (tr) and –158.5 (m) with intensity ratios 2:2:1:1:1:2 respectively.

Component B (0.5 g) recrystallized from light petroleum b.p. 60–80° to give *2-amino-nonafluorobenzophenone* (0.38 g) m.p. 103.5–104.5°. (Found: C, 43.3; H, 0.7; N, 3.8. C<sub>13</sub>H<sub>2</sub>F<sub>9</sub>NO requires: C, 43.5; H, 0.6; N, 3.9%). Mass spectrometry gave a top mass peak of 359 (required). The <sup>1</sup>H NMR spectrum (in CCl<sub>4</sub>) showed one signal at  $\delta$  7.1. The <sup>19</sup>F spectrum consisted of 7 signals with chemical shifts  $\delta$  –140.2 (d), –143.6 (m), –146.6 (d of tr's), –153.6 (tr), –161.0, –162.8 (both m's), and –175.8 (d of tr's) with intensity ratios 1:2:1:1:2:1:1 respectively.

(ii) *Stannous chloride.* To a soln of 2-nitro-nonafluorobenzophenone (0.6 g) in EtOH (30 ml) and water (7 ml) containing conc HCl (5 ml) was added SnCl<sub>2</sub> (1.0 g, SnCl<sub>2</sub> · 2H<sub>2</sub>O). The mixture was stirred at 50° for 4 h, then neutralized with 4N NaOH and extracted with ether (3 × 50 ml). The ethereal extracts were dried (MgSO<sub>4</sub>) and evaporated to give a residue (0.42 g) which was shown to be *perfluoro-3-phenyl-anthranil* by a comparison of IR spectra.

#### Electrolytic oxidation of 2-amino-nonafluorobenzophenone

The phenone (0.4 g) was electrolytically oxidized at an anode potential of +1.55–1.60 V (vs S.C.E.) at a platinum anode in an electrolyte of acetone (150 ml), water (260 ml) and potassium acetate (75 g) as previously described.<sup>1</sup> At the end of the electrolysis the anolyte was evaporated to remove acetone and the aqueous residue ether extracted (4 × 100 ml). The ethereal extracts were dried (MgSO<sub>4</sub>) and evaporated to give a product (0.45 g) which was purified by column chromatography (silica gel, EtOH eluant) to yield *octafluoroacridone* (0.15 g) m.p. 282–284° (dec). Found: C, 46.1; H, 0.7; N, 4.1. C<sub>13</sub>HF<sub>8</sub>NO requires: C, 46.0; H, 0.3; N, 4.1%.

Accurate mass measurement gave a top mass peak 338.992797 (required 338.993029). The IR spectrum showed strong bands at 1610 cm<sup>-1</sup> (>C=O) and approx 1500 cm<sup>-1</sup> (fluoroaromatic rings). The UV spectrum showed absorption maxima at  $\lambda_{\max}$  (EtOH) 2475, 2965, 3070, 3460, 3700 and 3850 Å ( $\epsilon$  58, 500, 5610, 7800, 6950, 8500 and 8500).

#### Pyrolysis of perfluoro-3-phenyl-anthranil

The anthranil (0.15 g) was heated at 235° for 12 h in a sealed tube, when the product was extracted with EtOH and filtered. The filtrate was evaporated to give a product (80 mg), which was refluxed with light petroleum b.p. 60–80°, filtered and evaporated. The residue (60 mg) was identified as *octafluoroacridone* by a comparison of IR spectra.

#### Electrolytic oxidation of 2-amino-2',3',4',5',6'-pentafluorobenzophenone

The phenone (2.9 g) prepared as previously described<sup>3</sup> was electrolytically oxidized as described above in the standard electrolyte (450 ml) at a potential of +1.4–1.5 V, and the anolyte extracted in the usual way. The product was sublimed under reduced pressure at 100–110° to give starting material (0.6 g), identified by IR spectroscopy. Further sublimation at 200° (0.05 mm Hg) gave 1,2,3,4-tetrafluoroacridone (0.55 g) identical with the compound previously described.<sup>3</sup> Further experiments showed that tetrafluoroacridone itself was susceptible to electrolytic oxidation at approx +1.5 V; no identifiable products were obtained.

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