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PRELIMINARY NOTE

Diazotisation of 4-Aminotetrafluoropyridine in a Sulphuric Acid-Acetic Acid-Propionic Acid Medium

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SUMMARY

4-Aminotetrafluoropyridine can be diazotised successfully by adding it to a solution of sodium nitrite in a mixture of 98% sulphuric acid, acetic acid and propionic acid; addition of mesitylene, *m*-cresol, 3,5-dimethylphenol or 2-naphthol to the solution of tetrafluoro-4-pyridyldiazonium ion thus produced provides the expected azo-compounds in good yields.

The recent disclosure [1] of a diazotisation technique for pentafluoroaniline that avoids use of hydrofluoric acid prompts us to report that we have made similar progress during our studies on coupling reactions of tetrafluoro-4-pyridyldiazonium ion [2].

In a typical diazotisation-coupling reaction, an 86:14 v/v mixture (20 cm<sup>3</sup>) of acetic and propionic acid was added dropwise to a stirred solution of dry sodium nitrite (0.7 g, 10 mmol) in 98% sulphuric acid (20 cm<sup>3</sup>) kept at < 30 °C by means of an ice bath; the nitrosating medium

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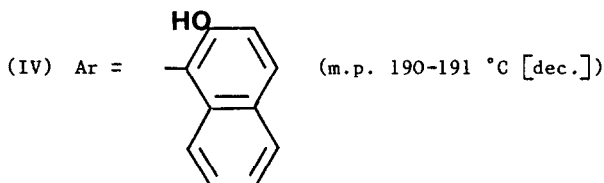
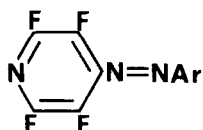
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thus produced was cooled to ca. 0 °C, treated with 4-aminotetrafluoropyridine (1.65 g, 10 mmol), then stirred at 0 °C for 3 hours (possibly an excessive period) before mesitylene (1.2 g, 10 mmol) was added dropwise. Immediately a red precipitate appeared, and after 3 more hours this was recovered (the reaction mixture was poured into water first) and purified by dry-column flash chromatography to provide the known [2] 4-(2,4,6-trimethylphenylazo)-2,3,5,6-tetrafluoropyridine (I) in 77% yield (2.3 g, 7.7 mmol). Similarly, the new azo-compounds (II)-(IV) were prepared by using m-cresol (yield 66%), 3,5-dimethylphenol (89%), or 2-naphthol (69%), respectively, as the coupling component instead of mesitylene. Use of concentrated sulphuric acid in conjunction with aliphatic carboxylic acids as a diazotisation medium for weakly-basic arylamines is a well-established technique [3].

(I) Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (m.p. 142-143 °C)

(II) Ar = 4-HOC<sub>6</sub>H<sub>3</sub>Me-2 (m.p. 172-173 °C)

(III) Ar = 4-HOC<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>-2,6 (m.p. 156-158 °C)



The new azo-compounds were identified by elemental analysis (C,H,F,N) and spectroscopic methods [i.r., mass, and n.m.r. (<sup>1</sup>H, <sup>19</sup>F)]; the mesitylene derivative (I) has been shown by X-ray crystallography [4] to prefer to exist in the trans-form, and the close correspondence between <sup>19</sup>F n.m.r. chemical shift data for members of the series (I)-(IV) indicates that the same is true for the other azo-compounds. Even in Manchester sunlight, trans-4-(2,4,6-trimethylphenylazo)tetrafluoropyridine (I) dissolved in deuteriochloroform isomerizes partly to the cis-form; after irradiation with u.v. light (through soda glass), a photostationary state was reached after 20 hours, the cis:trans ratio being 1:3 (establishment of equilibrium was followed by <sup>1</sup>H n.m.r.). Cis-trans photoisomerization of azo-compounds (II)-(IV) is under investigation, as is the possible occurrence of azo-hydrazone tautomerism.

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- 1 H. Iwamoto, T. Sonoda, and H. Kobayashi, *J. Fluorine Chem.*, 24 (1984) 535.
- 2 R.E. Banks, A.R. Thompson, and H.S. Vellis, *J. Fluorine Chem.*, 22 (1983) 499.
- 3 K.H. Saunders, 'The Aromatic Diazo-compounds and their Technical Applications', Arnold, London, 1936, p.11.
- 4 R.G. Pritchard, Personal Communication.