*Journal of Fluorine Chemistry, 22* (1983) 499–501

Received: February 4, 1983; accepted: February 10, 1983

PRELIMINARY NOTE

# Azo-Coupling of 2,3,5,6-Tetrafluoropyridine-4-Diazonium Fluoride with Mesitylene and Anisole

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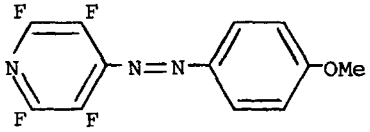
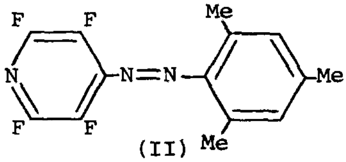
## SUMMARY



(I)



(II)

Anisole and mesitylene couple with tetrafluoropyridine-4-diazonium ion, generated by diazotisation of the corresponding amino-compound in 80% (by weight) aqueous hydrofluoric acid, to yield azo-dyes (I) and (II) respectively.

As discovered by Chambers et al. [1], addition of solid sodium nitrite to a cold (-20 °C) solution of the very weakly basic amine 4-aminotetrafluoropyridine in 80% (w/w) hydrofluoric acid provides tetrafluoropyridine-4-diazonium fluoride, which couples with NN-dimethylaniline to give 4-(NN-dimethylphenylazo)tetrafluoropyridine. Interestingly, we have now found that tetrafluoropyridine-4-diazonium ion is electrophilic enough to enter into coupling reactions with the phenolic ether anisole and the aromatic hydrocarbon

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0022-1139/83/$3.00

mesitylene, giving azo dyes (I) and (II), respectively. For example, sodium nitrite (8.5 mmole) was added during 15 min. to a cold (-20 °C) stirred solution of 4-aminotetrafluoropyridine (6.0 mmole) in hydrofluoric acid (40 $cm^3$; 80% w/w); after the temperature of the mixture had been lowered to -50 °C, anisole (6 mmole) was added. Work-up (after 1 hour) of the product [following ref.1] provided red crystals of 4-(4-methoxyphenylazo)-2, 3,5,6-tetrafluoropyridine (I) (2.9 mmole, 48%), m.p. 112 °C, which was characterised by elemental analysis (C,H,F and N) and spectroscopic methods [n.m.r. ($^1$H and $^{19}$F), mass, i.r. and u.v.]. 4-(2,4,6-Trimethylphenylazo)-2,3,5,6-tetrafluoropyridine (II), m.p. 143 °C, was prepared in a similar manner and isolated in 30% yield by column chromatography. Other products are formed besides azo dyes with all three coupling components ($C_6H_5NMe_2$ [<u>cf</u>.1], $C_6H_5OMe$, and 1,3,5-$C_6H_3Me_3$), and these are being examined.

4-(<u>NN</u>-Dimethylaminophenylazo)tetrafluoropyridine and its methoxyphenyl analogue (I) act as dyes towards nylon 6,6 but 4-(2,4,6-trimethylphenylazo)tetrafluoropyridine (II) does not. Of the first two, the methoxy-compound (I) has the higher light-fastness [rating 5 (according to B.S. 1006/1971; Xenotest 150 lamp) for 2 and 5% (w/w) dye bath strengths compared with rating 4 for 4-$Me_2NC_6H_4N{=}NC_5F_4N$-4].

The ability of tetrafluoropyridine-4-diazonium ion to effect eletrophilic substitution in (<u>i.e.</u> 'couple' with) an alkyl phenyl ether and an aromatic hydrocarbon is not unique [2]*, but the reactions described above appear to be the first yet reported where (<u>a</u>) a fluorinated aryldiazonium ion is involved and (<u>b</u>) that ion belongs to the pyridine class.

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*The best known of the relatively few previous cases where an aromatic hydrocarbon was employed as a coupling component involves attack on mesitylene by diazotised picramide (≡ 2,4,6-trinitrobenzendiazonium ion) [Meyer and Tochtermann].

## REFERENCES

1 R.D. Chambers, J. Hutchinson and W.K.R. Musgrave, J. Chem.Soc., (1965) 5040.

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