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PRELIMINARY NOTE

Synthesis of (Bistrifluoromethylamino-oxy)pyridines

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SUMMARY

The ready displacement of halide ion from various halogeno-, halogenonitro- and halogenocyano-pyridines by the salt $(CF_3)_2NO^-Na^+$ (II) provides a route to the corresponding (bistrifluoromethylamino-oxy)pyridines; 2-chloro- and 2-bromo-pyridine are unreactive under a variety of conditions.

4-(Bistrifluoromethylamino-oxy)tetrafluoropyridine (I) [1] {from treatment of pentafluoropyridine with the sodium salt of NN-bistrifluoromethylhydroxylamine (II) [2]} and 2-(bistrifluoromethylamino-oxy)pyridine (III) [3] {from reaction of 2-chloropyridine with a mixture of mercury (I) and mercury (II) bistrifluoromethylnitroxide of approximate composition $[(CF_3)_2NO]_{1.3}Hg$ at 50 °C} are the only pyridines reported bearing the $(CF_3)_2NO$ group as a nuclear substituent. The mercurial failed to convert 3-chloropyridine into 3-(bistrifluoromethylamino-oxy)pyridine [4].

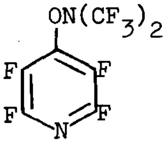
The ready displacement of halide ion by the salt (II) [5] from various halogenonitrobenzenes to give the corresponding (bistrifluoromethylamino-oxy)nitrobenzenes [6] prompted an investigation of the reaction of the salt (II) with halogenopyridines; the results obtained are shown in the Table.

TABLE

Reaction of the sodium salt (II) with some halogenopyridines

Pyridine	Ratio of salt (II):pyridine	Pyridine (mmol)	Solvent (cm^3)	Temp. (°C)	Time (h)	Product	Yield	Conversion
2-fluoropyridine	1:1	10	$(CF_3)_2NOH$ (5)	100	5	(III)	18.5	54
2,5-dibromopyridine	1:1	20	DMF (25)	110	2	(IV)	94	43
2-chloro-3-nitropyridine	1:1	14.5	THF (30)	20	18	(V)	100	85
	1:1	21	DMF (30)	90	12	(V)	99	79
2-chloro-5-nitropyridine	1:1	33	THF (25)	64	24	(VI)	100	100
	1:1	9	DMF (25)	70	4	(VI)	100	100
2-chloro-3-cyano-4,6-dimethylpyridine	1:1	9	THF (25)	66	15	(VII)	100	50
	2:1	10	THF (25)	66	12	(VII)	83	100
4-chloropyridine	2:1	10	DMSO (25)	100	4	(VIII)	21	38*
_N_-(4-pyridyl)-pyridinium chloride hydrochloride	2:1	23	DMF (25)	100	21	(VIII)	87	100

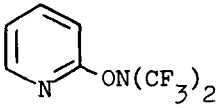
* 4-Chloropyridine (62%) also obtained after work up.



(I)

$(CF_3)_2NO^-Na^+$

(II)



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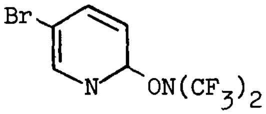

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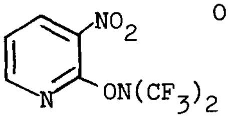

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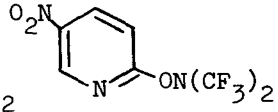
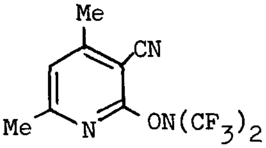
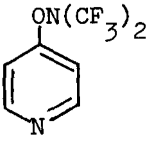


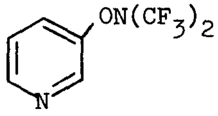
(VI)



(VII)



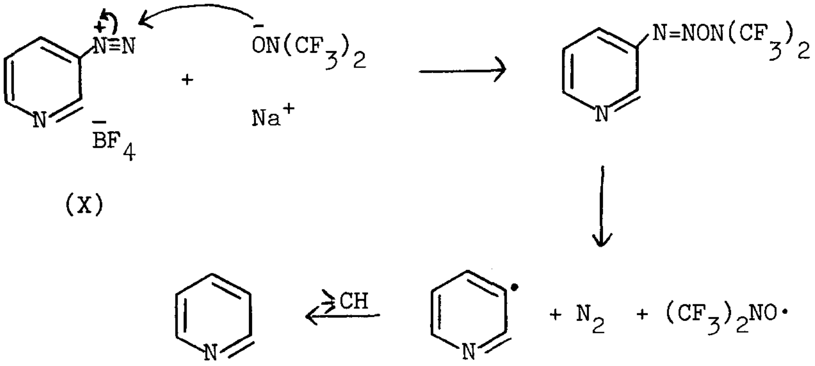
(VIII)



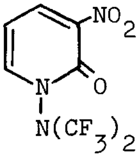
(IX)

The sodium salt (II) was unreactive towards 2-chloro- and 2-bromo-pyridine under a variety of conditions demonstrating that it is a relatively weak nucleophile.

An alternative synthesis of 3-(bistrifluoromethylamino-oxy)pyridine (IX) was then sought and it was found that treatment of pyridine-3-diazonium tetrafluoroborate (X) with the salt (II) in dry acetonitrile gave compound (IX), albeit in low yield (12.5%). However, on repeating the reaction in dry THF as solvent, pyridine (92%) was obtained which is envisaged as arising *via* a modified Gomberg mechanism [7], *i.e.*



The static pyrolysis of pyridine (V) at 130 °C (60h) gave the novel 1-(bistrifluoromethylamino)-3-nitro-2-pyridone (XI) (30%).



(XI)

The structures of the products were established spectroscopically [i.r., n.m.r. (^1H and ^{19}F) and mass] and all possessed correct elemental compositions.

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1 R.E. Banks, R.N. Haszeldine, and D.L. Hyde, Chem.Comm., (1967) 413.

2 The salt (II) was prepared *in situ* from the hydroxylamine $(CF_3)_2NOH$ and powdered sodium hydroxide in THF in the presence of a molecular sieve to remove water.

3 R.E. Banks, C.M. Irvin, and A.E. Tipping, J. Fluorine Chem., (1980) in the press.

4 R.E. Banks, C.M. Irvin, and A.E. Tipping, unpublished results.

5 The salt (II) as used both in the halogen-displacement reactions described in reference 6 and in the present work, was prepared by treatment of the parent hydroxylamine with sodium hydride in diethyl ether followed by removal of the ether by evaporation and then redissolution of the solid salt in the appropriate solvent, a method pioneered by R.E. Banks and R.A. Hughes in this Department.

6 R.E. Banks, A.K. Brown, R.N. Haszeldine, A. Kenny, and A.E. Tipping, J. Fluorine Chem., (1980) in the press.

7 M. Gomberg and W.E. Bachmann, J.Amer.Chem.Soc., *46* (1924) 2339.