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PRELIMINARY NOTE

Reaction of Sodium Diethylnitroxide with Fluorobenzenes, Pentafluoropyridine and Halogenopyridines

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SUMMARY

Treatment of pentafluoropyridine with sodium diethylnitroxide in diethyl ether gave tetrafluoropyridines 4-RC_5F_4N (R = $ONEt_2$, NEt_2, NHEt and $O^- H_2\overset{+}{N}Et_2$); in the presence of p-dinitrobenzene only the hydroxylamine (R = $ONEt_2$) was detected. Octafluorotoluene afforded analogous products with the exception of the amine 4-CF_3-C_6F_4-NEt_2, while from the pentafluorobenzene reaction only the salt 4-H-C_6F_4-$O^-H_2\overset{+}{N}Et_2$ was isolated. In contrast the reactions involving 2-chloro-3-nitro- and 2-chloro-5-nitro-pyridine yielded the 2-diethylamino derivatives and bis(pyridyl)amines.

Reaction of the salt $(CF_3)_2NO^-Na^+$ with chloronitrobenzenes [1], octafluorotoluene [2], 2- and 4-halogenopyridines [2,3] and polyfluoropyridines [2,4] yields, in all cases, the expected bis(trifluoromethyl)amino-oxy derivatives via a presumed S_NAr pathway. Replacement of chlorine by the $(CF_3)_2NO$ group in 2-chloro-pyridine, -pyrimidine and -pyrazine has also been effected using mercurials derived from bistrifluoromethyl nitroxide [5]. However, capture of benzyne (generated from anthranilic acid and isoamyl nitrite) with the hydroxylamine $(CF_3)_2NOH$ affords the novel amine oxide **(1)** and the amine **(2)** [1].

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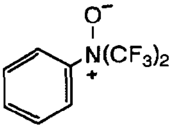
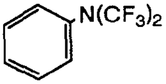


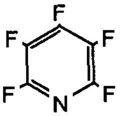
(1)



(2)

$Et_2NO^-Na^+$

(3)



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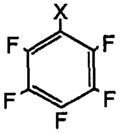
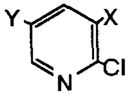
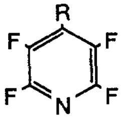


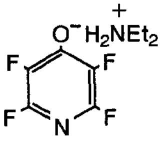
(5) $X=CF_3$
(6) $X=H$



(7) $X=NO_2$, $Y=H$
(8) $X=H$, $Y=NO_2$



(9) $R=NEt_2$
(10) $R=ONEt_2$
(11) $R=NHEt$



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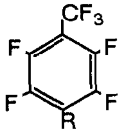
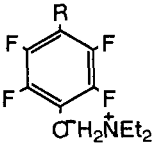
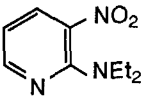


(13) $R=ONEt_2$
(14) $R=NHEt$



(15) $R=CF_3$
(16) $R=H$



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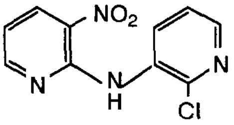

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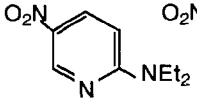

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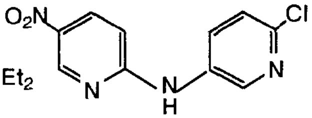

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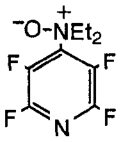

(21)

Although a number of N-fluoroaryl- and N-fluoropyridyl-hydroxylamines have been reported [6-8], O-fluoroaryl- and O-fluoropyridyl-hydroxylamines [apart from those containing the $(CF_3)_2NO$ group] are conspicuous by their absence from the chemical literature. In an attempt to rectify this situation, reactions between sodium diethylnitroxide **(3)** and pentafluoropyridine **(4)**, octafluorotoluene **(5)** and pentafluorobenzene **(6)** have been investigated and, for comparison, reactions involving 2-chloro-3-nitropyridine **(7)** and 2-chloro-5-nitropyridine **(8)** have also been carried out. The reaction conditions and the products obtained are shown in the Table.

TABLE

Reaction of sodium diethylnitroxide **(3)**[a] with polyfluorobenzenes and halogenopyridines in anhydrous diethyl ether

Substrate	(mmol)	**(3)** (mmol)	Conditions	Products [yield/%][b]
(4)	44.4	43.5	15h, -78 °C	**(9)** [trace], **(10)**[33][c], **(11)**[8], **(12)** [4]
(4)	89.0	87.0	24h, 0 °C	**(9)** [trace], **(10)**[23][c], **(11)** [21], **(12)** [3]
(5)	42.4	41.7	8 h, -78 °C	**(13)** [23], **(14)** [2] **(15)** [12]
(6)	49.0	48.5	200 h, 20 °C	**(16)** [15]
(7)	19.0	18.7	72 h, 20 °C	**(17)** [35], **(18)** [13]
(8)	9.0	18.7	24 h, 20 °C	**(19)** [25], **(20)** [22]

[a] The salt **(3)** was made by treatment of N,N-diethylhydroxylamine with sodium in anhydrous diethyl ether.

[b] Intractable tar was also formed in the reactions.

[c] Compound **(10)** decomposes to give the salt **(12)** and tar on storage.

Treatment of pentafluoropyridine **(4)** with the salt **(3)** in the presence of p-dinitrobenzene (a free-radical quencher) in diethyl ether at 20 °C for 24 hours gave only the hydroxylamine **(10)** together with products derived from the dinitrobenzene; compounds **(9)**, **(11)** and **(12)** were not detected, and consumption of the salt **(3)** occurred more slowly than in the absence of the quenching agent.

It is therefore considered that two mechanisms are operative in the reaction involving substrates **(4-6)**: (i) a one-electron transfer from salt **(3)** to the substrate (radical intermediates were also confirmed by e.s.r.) which can lead to all the isolated products and (ii) an S_NAr mechanism leading to the diethylamino-oxy derivatives (and the salts by decomposition).

One of the intermediates expected to result from a one-electron transfer mechanism is the amine oxide $Et_2\overset{+}{N}(Ar)O^-$, e.g. **(21)**. Pyrolysis of compound **(21)** [prepared independently by oxidation of the amine **(9)** with $(CF_3CO)_2O/H_2O_2$ (85%)] gave compounds **(10)** (58%) and **(11)** (12%).

The amines **(17)** and **(19)** isolated from the products of reactions between **(3)** and chloronitropyridines **(7)** and **(8)**, respectively, probably result from deoxygenation of the intermediate amine oxides, while the bis(pyridyl)amines **(18)** and **(20)** can be accounted for by reduction ($NO_2 \rightarrow NH_2$) followed by nucleophilic displacement of chlorine from a second molecule of substrate by the amines $PyNH_2$.

The mechanisms of these reactions and the chemistry of certain of the products will be discussed at length in a full paper.

The structures of all the products were established spectroscopically [i.r., n.m.r. (^1H, ^{13}C, ^{19}F) and mass] and, apart from compounds **(14-16)** which were not analysed, they possessed satisfactory elemental compositions.

We thank the Committee of Vice Chancellors and Principals for an O.R.S. award (to W.J.).

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