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PRELIMINARY NOTE

Preparation of (Bistrifluoromethylamino)pyridines

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SUMMARY

The reactions of perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (III) with pyridine and halogenopyridines affords novel (bistrifluoromethylamino)pyridines; the product orientation is consistent with initial attack on the ring by the highly electrophilic $(CF_3)_2N\cdot$ radical.

Various routes to (bistrifluoromethylamino)benzenes have been described [1-5], but the only heteroaromatic compounds reported which contain nuclear $(CF_3)_2N$ groups are the triazine derivatives (I) [6] and [(II), X=Y=Z=N$(CF_3)_2$; X=F, Y=Z=N$(CF_3)_2$; X=N$(CF_3)_2$, Y=Z=F][7] prepared by reaction of the salt CsN$(CF_3)_2$ with cyanuric chloride and trifluoro-1,2,4-triazine, respectively.

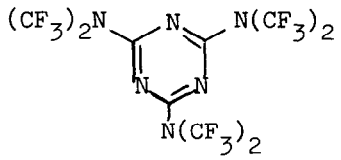
The recent discovery that reaction of perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane)(III) with benzene and various substituted benzenes afforded a novel one-stage route to $(CF_3)_2N$-substituted benzenes [5] prompted an investigation of the reaction of the oxadiazapentane (III) with pyridine and some halogenopyridines. The results obtained are summarised in the Table.

TABLE

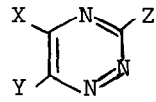
Reaction of the oxadiazapentane (III) with pyridines C_5H_4XN[1]

Pyridine		(III)	Conditions		Pyridine	(III)	Products[2]
X	(mmol)	(mmol)	Temp. (°C)	Time (h)	recov.(%)	recov.(%)	(%)
H	10.0	11.5	50	12	35	27.5	(IV) (32)
H[3]	35.1	55.3	55	24	38	62	(IV) (60) (V) (7)
2-Cl	10.6	10.7	70	48	34		(VI) (28.5) (VII) (27)
3-Cl	9.8	11.6	70	12	47	16.5	(VIII) (48) (IX) (18.5) (X) (18.5)
2-F	10.1	10.5	70	24	21.5	25	(XI) (10) (XII) (32.5) (XIII) (41.5)
3-F	9.7	10.2	70	12	69	33	(XIV) (57)[4]

1 Reactions were carried out in sealed tubes (100 cm^3 capacity unless stated otherwise). 2 The compounds $(CF_3)_2NH$ and $(CF_3)_2NOH$ and solid unidentified residues were also formed. 3 This reaction employed a larger tube (300 cm^3) and the oxyl $(CF_3)_2NO\cdot$ (20%) was also isolated. 4. An unidentified product (ca. 25%) was also formed which decomposed to give 3-fluoropyridine on attempted g.l.c. separation.



(I)



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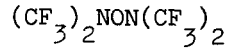

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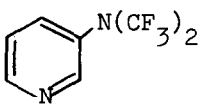

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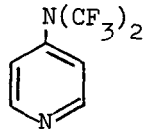

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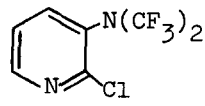

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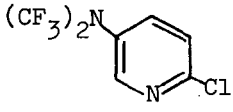

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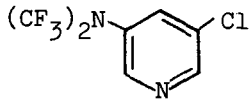

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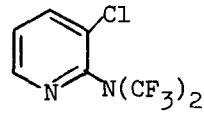

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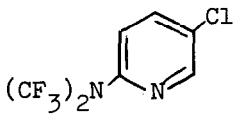
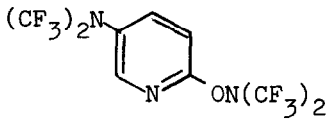
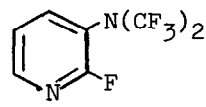


(X)



(XI)



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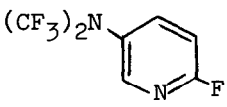
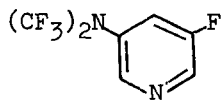


(XIII)



(XIV)

The results obtained previously from reaction of the oxadiazapentane (III) with benzene derivatives suggested that the $(CF_3)_2N$-substituted benzenes were formed *via* attack of the highly electrophilic $(CF_3)_2N\cdot$ radical on the ring [5]. The results obtained in the present work are in agreement with this. Thus a radical pathway is indicated by the isolation of the oxyl $(CF_3)_2NO\cdot$ from the larger-scale pyridine reaction and the major products from all the reactions studied contained a $(CF_3)_2N$- substituent in the 3- or 5-position as expected for electrophilic attack with the ring nitrogen having the major effect in determining the orientation of attack.

It was found previously from the chlorobenzene reaction [5] that the chlorine atom had a strong *para*-directing effect; no such effect was observed in the reactions involving 2- and 3-chloropyridine.

The structures of the products were established spectroscopically [i.r., n.m.r. (^1H and ^{19}F), and mass] and all the products possessed correct elemental compositions except compound (V) which was not analysed.

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